

# Chemistry Revision Themes

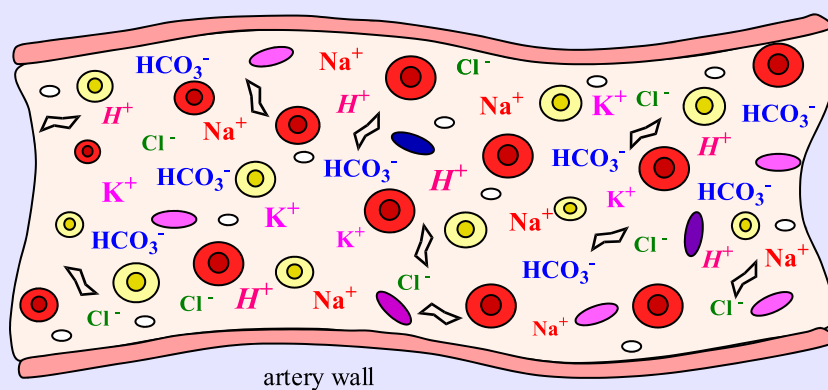
## Part IIIa

Themes:

**Organic Chemistry III**

**Acid-Base Equilibria**

**Redox Equilibria**



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 (NB: Consult *your* examining board syllabus to establish precise requirements)

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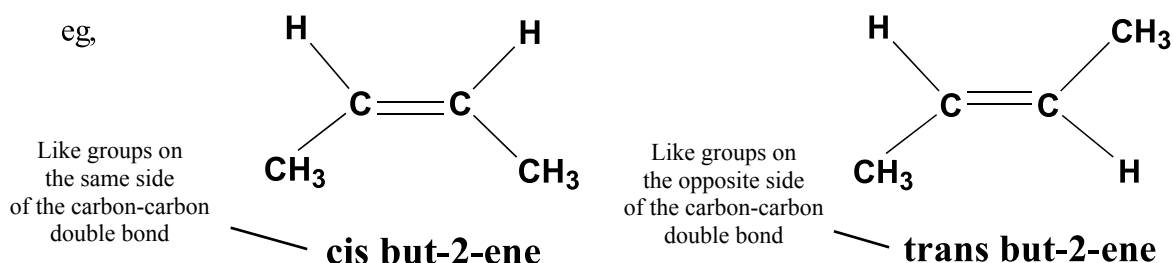
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# Theme Twelve

## Organic Chemistry III

### Stereoisomerism

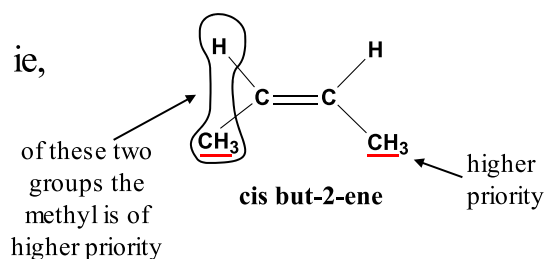
(i) **Geometrical Isomerism:** This is where molecules have the same molecular formula and the same structural formula but different molecular geometries (shapes). Alkenes in which the unsaturated carbon atoms are attached to different atoms or groups provide simple examples of geometrical isomers.



The prefixes, *cis* and *trans* are frequently used to distinguish geometrical isomers by name. However, a more modern system is also employed based on the [Cahn-Ingold-Prelog system](#).

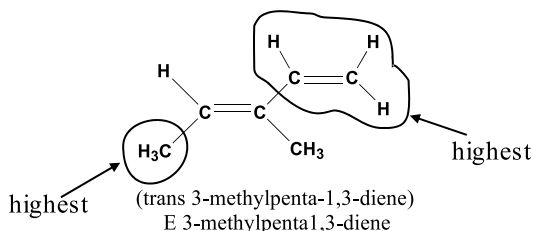
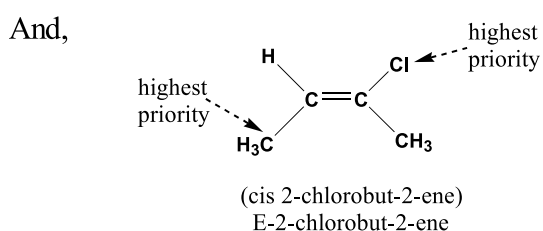
An order of priority is established based on atoms of higher atomic number taking precedence over those of lower atomic number.

Consider the case of *cis* but-2-ene. On each of the unsaturated carbon atoms, carbon (in the methyl group) is of higher priority than hydrogen.



Since the two groups of highest priority are on the same side of the double bond the structure is called **Z-but-2-ene** where Z derives from the German word, *zusammen*, meaning together.

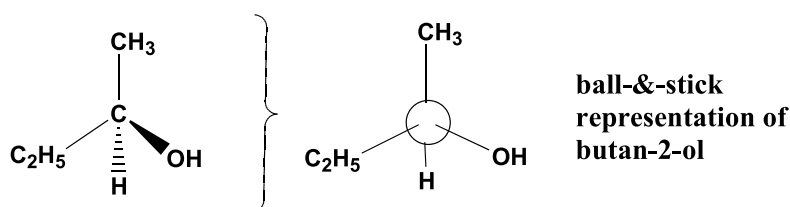
Trans but-2-ene is called **E-but-2-ene**. Where E derives from the German, *entgegen*, meaning opposite.



## Optical Isomerism

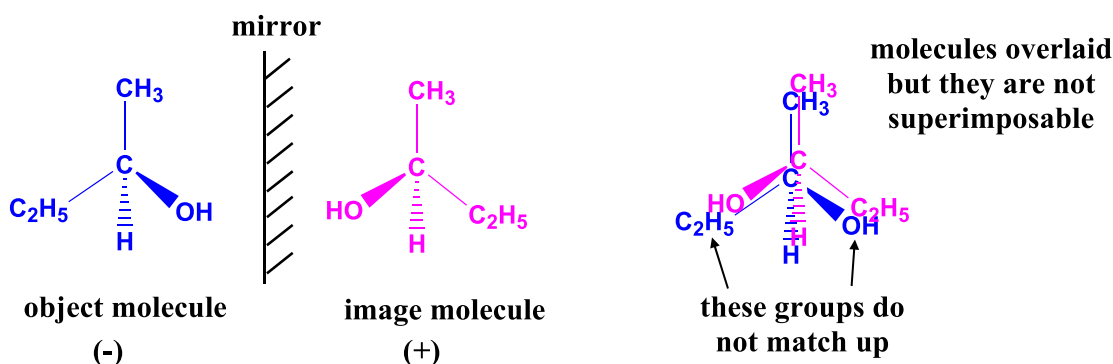
Another type of stereoisomerism is called **optical isomerism**. Optical isomers do not have a plane of symmetry and can be recognised by their ability to rotate the plane of **plane polarised** light (ie, vibrating in just one plane).

A simple example of a substance which exhibits optical isomerism is butan-2-ol. Molecules of this substance have a central carbon atom which has four different groups attached to it; this carbon atom is said to be **asymmetric**. As a result of this centre of asymmetry the molecule, as a whole, lacks a plane of symmetry and is said to be **chiral** (from the Greek word, *cheir* meaning *hand*).



Molecules with this structure are laevo rotatory (laevo, from the Latin for left) because they will rotate plane polarised light to the left. This may be indicated in the name with a negative sign, ie., (-)-butan-2-ol.

The interesting feature of this molecule is that its **mirror image** is structurally different. Its mirror image is non-superimposable on the original structure.

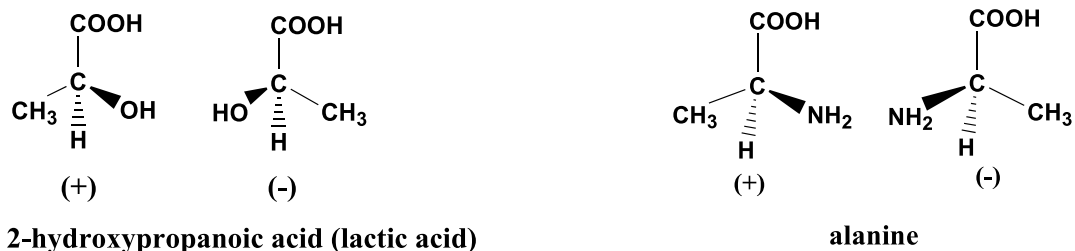


These molecules can be distinguished because the 'object' molecule will rotate plane polarised light to the left (laevo rotatory) whilst the 'image' molecule will rotate the light to the right (dextro rotatory). The mirror image structures are known as **enantiomers**.

Synthesised butan-2-ol does not affect plane polarised light. This is because the synthesised material is a 1:1 mixture of the enantiomers (the (+) and (-) forms). It is referred to as a **racemic mixture**.



Some further examples of optical isomers:

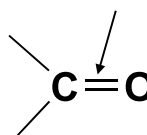


The measurement of the angle of rotation would be made using a simple optical instrument called a *polarimeter*.

## Carbonyl Compounds

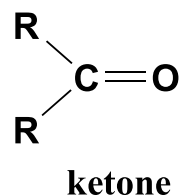
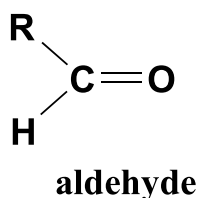
These organic compounds contain the carbonyl group:

**carbon-oxygen  
double bond**



In **aldehydes** and **ketones** this is the principal group.

ie,



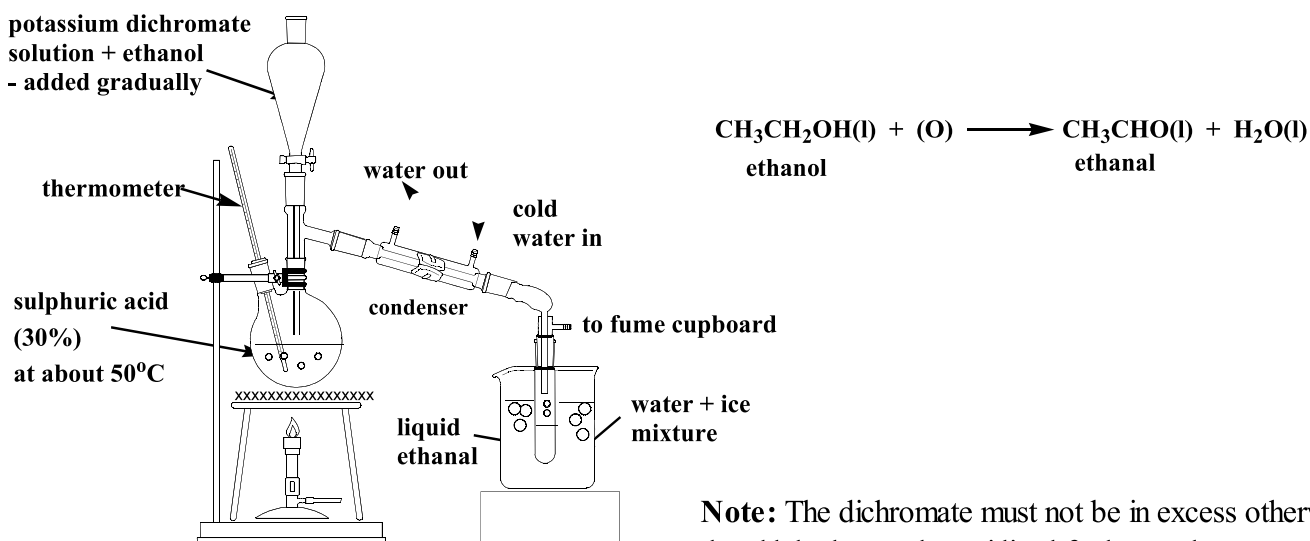
Where R is an alkyl group. In a ketone the two alkyl groups may be the same or different.

Some examples:

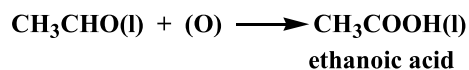
Modern Name	Common Name	Formula
<b>Aldehydes</b>		
Methanal	Formaldehyde	HCHO
Ethanal	Acetaldehyde	CH <sub>3</sub> CHO
Propanal	Propionaldehyde	CH <sub>3</sub> CH <sub>2</sub> CHO
Butanal	Butyraldehyde	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CHO
<b>Ketones</b>		
Propan-2-one	Acetone	(CH <sub>3</sub> ) <sub>2</sub> CO
Butan-2-one	Ethyl methyl ketone	(C <sub>2</sub> H <sub>5</sub> )(CH <sub>3</sub> )CO
Pentan-3-one	Diethyl ketone	(CH <sub>3</sub> CH <sub>2</sub> ) <sub>2</sub> CO
Pentan-2-one	Methyl propyl ketone	(CH <sub>3</sub> )(C <sub>3</sub> H <sub>7</sub> )CO

Both groups of carbonyl compounds can be made by oxidising alcohols with a solution of potassium dichromate acidified with dilute sulphuric acid.

## Apparatus required for the Laboratory Preparation of Ethanal:

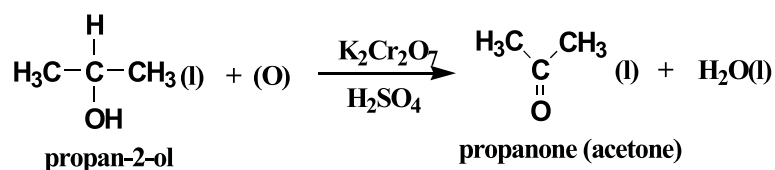


**Note:** The dichromate must not be in excess otherwise the aldehyde may be oxidised further to the corresponding carboxylic acid.

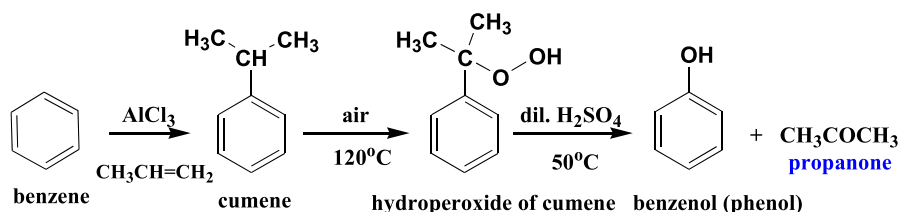
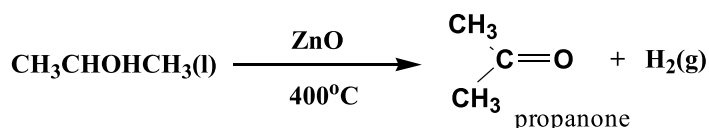
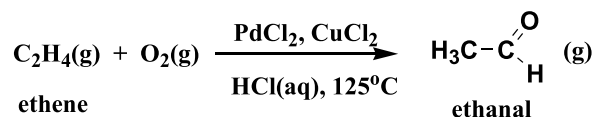
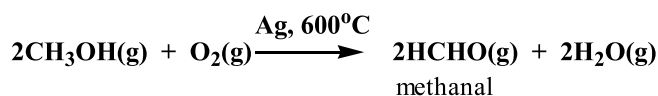


A ketone is obtained by oxidising a secondary alcohol (i.e., one containing the -CHOH- group).

e.g.,

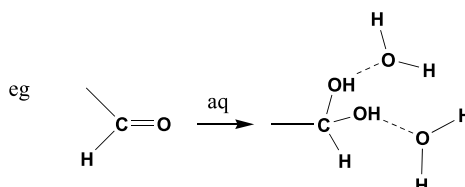


Diverse oxidation processes are used to synthesise carbonyl compounds on a large scale.  
eg,



## Properties of Aldehydes and Ketones

The carbonyl group in aldehydes is more polarised and less sterically hindered than that in ketones; as a result, aldehydes are generally more reactive than ketones. Simple carbonyl compounds are soluble in water. Some hydration of the carbonyl group occurs enhancing hydrogen bonding with water molecules.

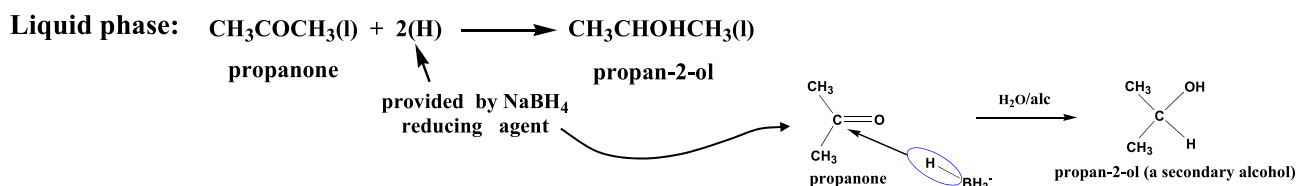
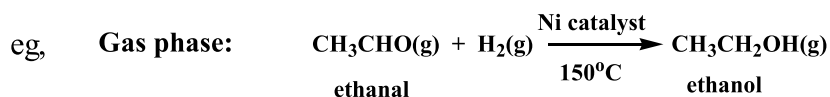


### Reduction:

Aldehydes and ketones can be reduced to the corresponding alcohol. **Aldehydes give primary alcohols whereas ketones give secondary alcohols.**

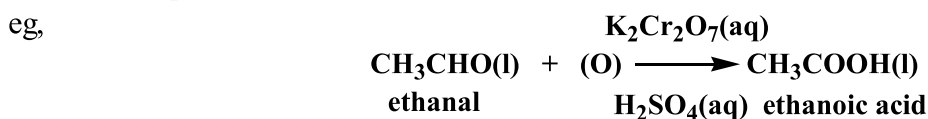
Reactions can be performed in either the gas phase or liquid phase (eg, aqueous solution).

## Organic Chemistry III



## Oxidation:

Aldehydes are readily oxidised to the corresponding carboxylic acid by warming with dichromate solution acidified with dilute sulphuric acid.

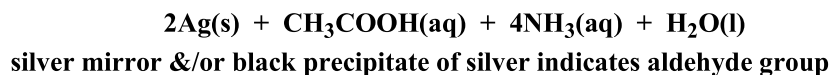
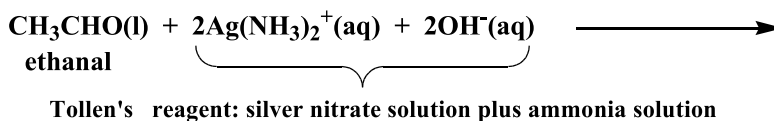


Ketones are more difficult to oxidise and are *not* oxidised using acidified dichromate solution.

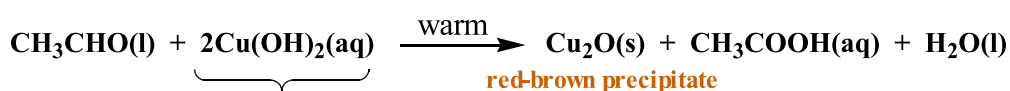
Mild oxidising agents are used to test for and distinguish aldehydes and ketones.

*With the following reagents only aldehydes give a positive result:*

### Tollen's reagent:



### Fehling's reagent:

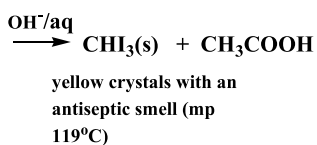
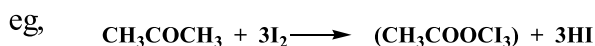


Fehling's reagent: alkaline copper sulphate containing sodium potassium tartrate

## With Iodine:

The iodoform reaction.

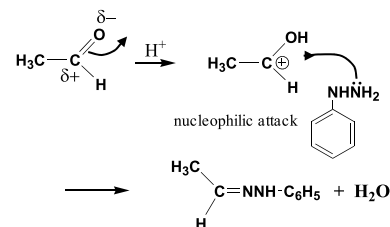
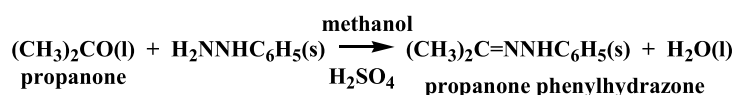
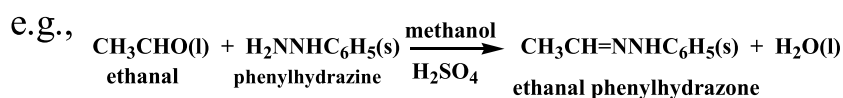
Aldehydes and ketones, containing the groups, CH<sub>3</sub>COC- or CH<sub>3</sub>CHOH- give yellow crystals of iodoform (CHI<sub>3</sub>) when warmed with iodine in aqueous sodium hydroxide.



This reaction provides a useful test for CH<sub>3</sub>CO and CH<sub>3</sub>CHOH groups. Propanone, butanone, pentan-2-one and phenylethanone all give a positive result. Methanal, diphenylmethanone and pentan-3-one do not. Ethanal (CH<sub>3</sub>CHO) gives a positive result, in aqueous solution, because in aqueous solution it is hydrated, CH<sub>3</sub>CH(OH)<sub>2</sub>.

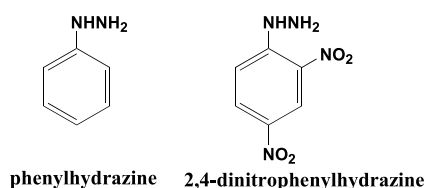
## 2,4-Dinitrophenylhydrazine reagent (2,4-DNP):

Carbonyl compounds undergo **condensation reactions**. In these reactions two products are formed one of which is a simple substance such as water or ammonia.



Reactions of this type are useful as a means of identifying particular aldehydes and ketones. The phenylhydrazone condensation products are brightly coloured (yellow or orange) and insoluble under the conditions of the reaction and may be filtered off and recrystallised from a suitable solvent. The pure, dry, material melts at a specific temperature which is characteristic of the condensation product and also of the original aldehyde or ketone.

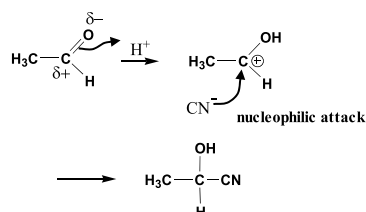
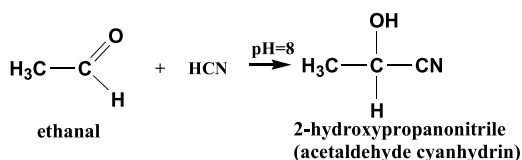
**In practice, 2,4-dinitrophenylhydrazine rather than phenylhydrazine is reacted with the carbonyl compounds because it produces derivatives with sharper, more reliable, melting points.**



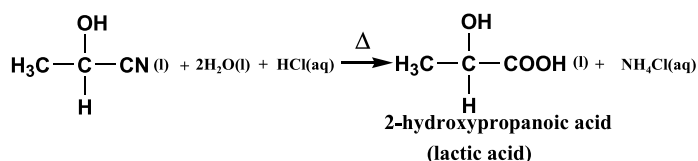
2,4-DNP in methanol plus concentrated sulphuric acid is often referred to as **Brady's reagent**.

## With Hydrogen Cyanide

Addition reactions of aldehydes and ketones, involving hydrogen cyanide, result in the formation of compounds called **cyanhydrins**.



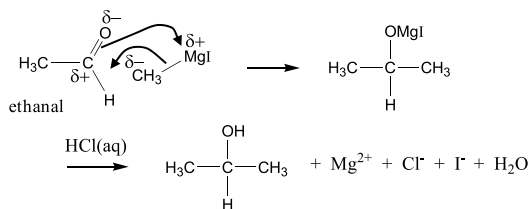
The cyanide group (also known as a **nitrile** group, -CN) is readily hydrolysed to a carboxylic acid group.



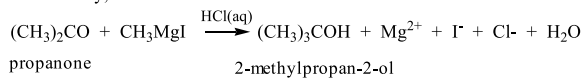
## Grignard Reagents:

Grignard reagents are organomagnesium compounds made by reacting magnesium turnings with haloalkane in dry ether. They react readily with carbonyl compounds producing addition compounds which are readily hydrolysed to an alcohol. Aldehydes give secondary alcohols, ketones give tertiary alcohols.

eg,



Similarly,



## Applications of Methanal, Ethanal and Propanone

The majority of the methanal (formaldehyde) manufactured is used for making synthetic resins, e.g., Delrin, melamine and phenol-formaldehyde resins.

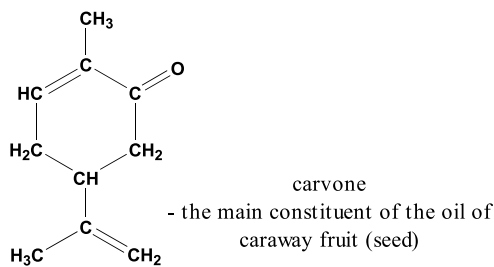
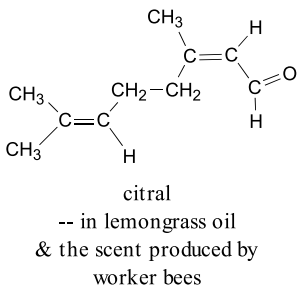
Ethanal (acetaldehyde) is used to make ethanoic acid, ethanoic anhydride, butanol, pentaerythritol (i.e.,  $\text{C}(\text{CH}_2\text{OH})_4$  - used in the manufacture of polyester resins) and but-2-enal (crotonaldehyde,  $\text{CH}_3\text{CH}=\text{CHCHO}$ ).

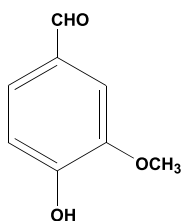
Propanone (acetone) is used as a solvent for paints, varnishes, lacquers and cellulose acetate. It is also used to make other solvents, methyl methacrylate and drugs.

## Carbonyl Compounds in Nature

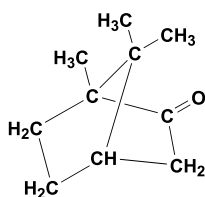
Aldehydes & ketones are produced by both plants and animals. The aldehydes are labile however since they are readily oxidised to the corresponding acids.

Examples:

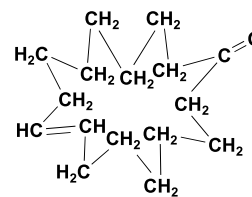




vanillin - major component of vanilla bean oil



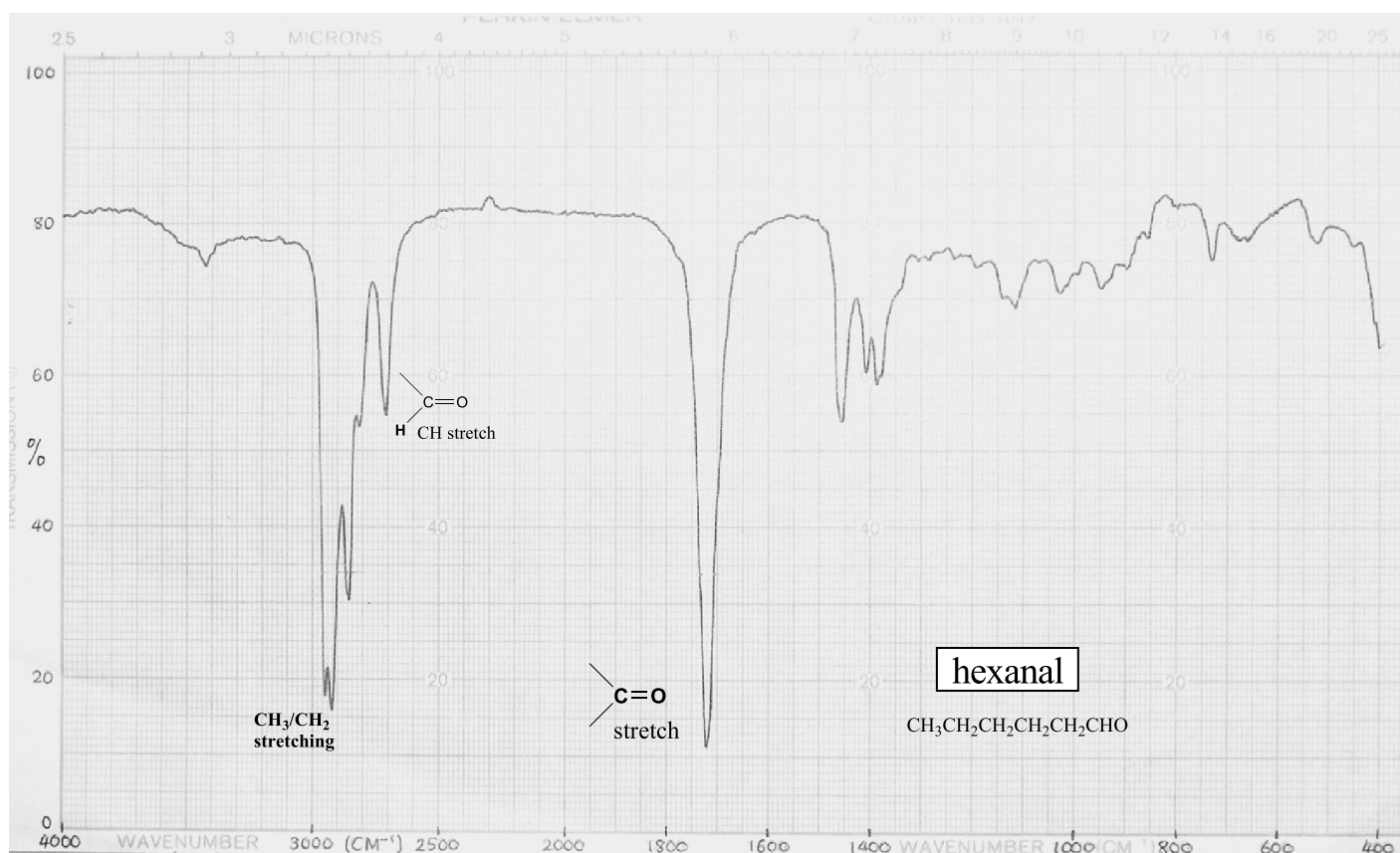
camphor - a nasal decongestant from the camphor tree native to Japan and China.



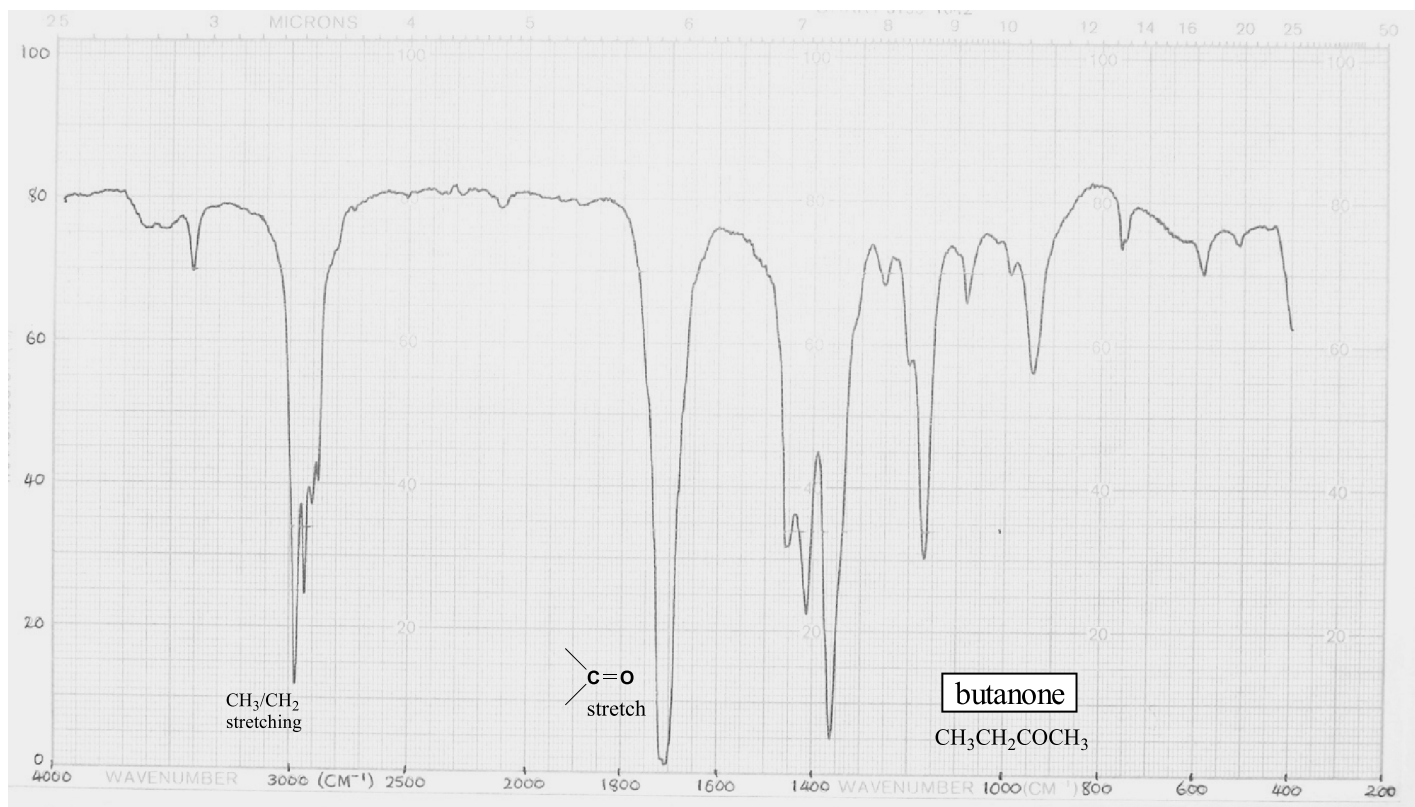
civetone - produced by the civet cat, a valued perfumery product

## Infra-red spectra of carbonyl compounds

The carbonyl group absorbs strongly in the region of  $1700\text{ cm}^{-1}$ . Aldehydes also show medium absorption at  $2720\text{ cm}^{-1}$  due to C-H stretch in the aldehyde group. This latter absorption often enables aldehydes to be distinguished from ketones.







## Carboxylic Acids

### Properties:

Organic acids containing one carboxyl group are called monocarboxylic acids. They form a homologous series.

Modern name	Formula	Common name
methanoic acid	<b>HCOOH</b>	formic acid
ethanoic acid	<b>CH<sub>3</sub>COOH</b>	acetic acid
propanoic acid	<b>C<sub>2</sub>H<sub>5</sub>COOH</b>	propionic acid
butanoic acid	<b>C<sub>3</sub>H<sub>7</sub>COOH</b>	n-butyric acid
pentanoic acid	<b>C<sub>4</sub>H<sub>9</sub>COOH</b>	n-valeric acid

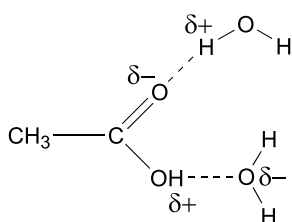
CH<sub>3</sub>COOH has the modern name, **ethanoic acid**.

*ethan* from ethane  
indicating 2 carbon  
atoms

**-oic** referring  
to -COOH

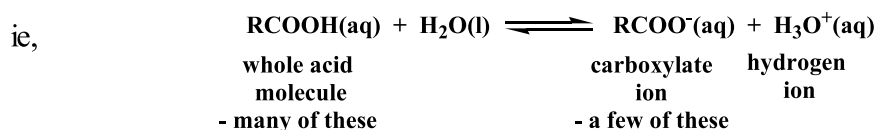
The simple members of the monocarboxylic group are freely soluble in water.

Solubility is enhanced by extensive hydrogen bonding involving the carboxyl group and water molecules.





Carboxylic acid solutions are weakly acidic. The reason for this is that the acid molecule does not readily dissociate (i.e., break up into ions) in aqueous solution.



The acid-base indicators can be used to demonstrate the acidity of solutions of carboxylic acids.

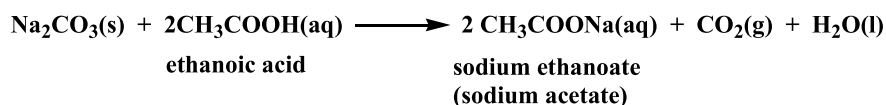
A dilute solution of ethanoic acid (acetic acid) will turn blue *litmus* paper red.

The indicators, *methyl orange* and *methyl red* show red in dilute carboxylic acid solutions. *Bromothymol blue* gives a yellow colour in these acid solutions.

## Sodium carbonate

When sodium carbonate (washing soda), either as the solid or in solution, is added to a solution of a carboxylic acid a reaction ensues with vigorous evolution of carbon dioxide.

e.g.,



Notice that it is the hydrogen in the carboxyl group (i.e., the hydrogen atom which is directly bonded to oxygen) which is most reactive (acidic) and replaced by sodium. The reaction is used as a simple test for carboxylic acids.

Sodium hydrogencarbonate also reacts with carboxylic acids giving carbon dioxide and the sodium salt of the acid.

## Metals

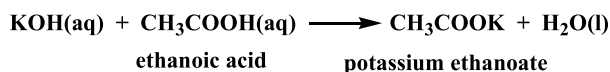
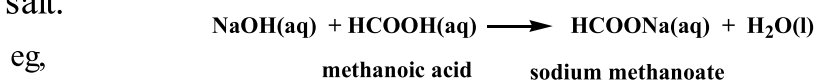
The alkali metals react readily with carboxylic acids forming the corresponding salt. The heavier metals react slowly or not at all.

Magnesium shows moderate reactivity with a solution of ethanoic acid producing hydrogen and magnesium ethanoate.



## Strong Bases

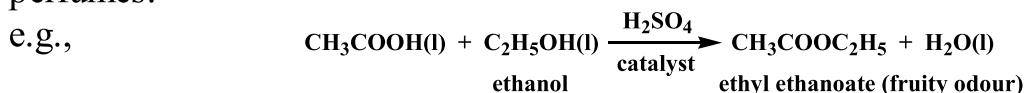
Sodium and potassium hydroxides react readily with carboxylic acids forming the corresponding salt.



## Alcohols

In the presence of a few drops of concentrated sulphuric acid, carboxylic acids react with alcohols to form **organic esters** (*inorganic esters* are the compounds formed when inorganic acids (eg.,  $\text{HBr}$ ,  $\text{H}_2\text{SO}_4$ ) react with alcohols).

The simple organic esters are pleasant smelling, organic compounds, used as solvents and as perfumes.

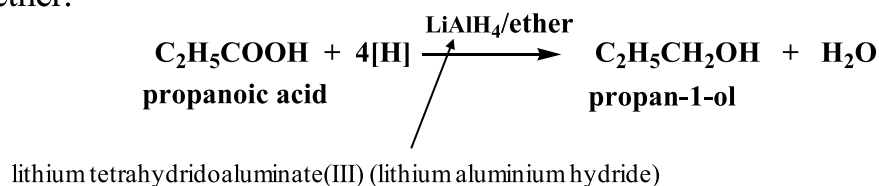


This reaction may be used as a test for carboxylic acids and/or alcohols. Very often esters have characteristic odours which can be used to identify them.

e.g., methyl butanoate (  $\text{C}_3\text{H}_7\text{COOCH}_3$  ) has an apple odour and iso-amyl ethanoate (  $\text{CH}_3\text{COOCH}_2\text{CH}_2\text{CH}(\text{CH}_3)_2$  ) a pear odour.

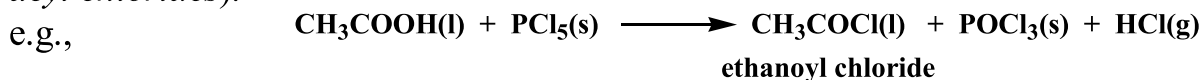
## Reducing agent

The carboxylic acid group is difficult to reduce, however, the powerful reducing agent lithium aluminium hydride will convert the carboxyl group to primary alcohol. The reaction is carried out in dry ether.



## Phosphorus pentachloride

Carboxylic acids react with phosphorus pentachloride forming **acid chlorides** (also called *acyl chlorides*).



Methanoic acid, is an exception amongst carboxylic acids, it does not form an acid chloride with phosphorus pentachloride.

## Preparation of carboxylic Acids

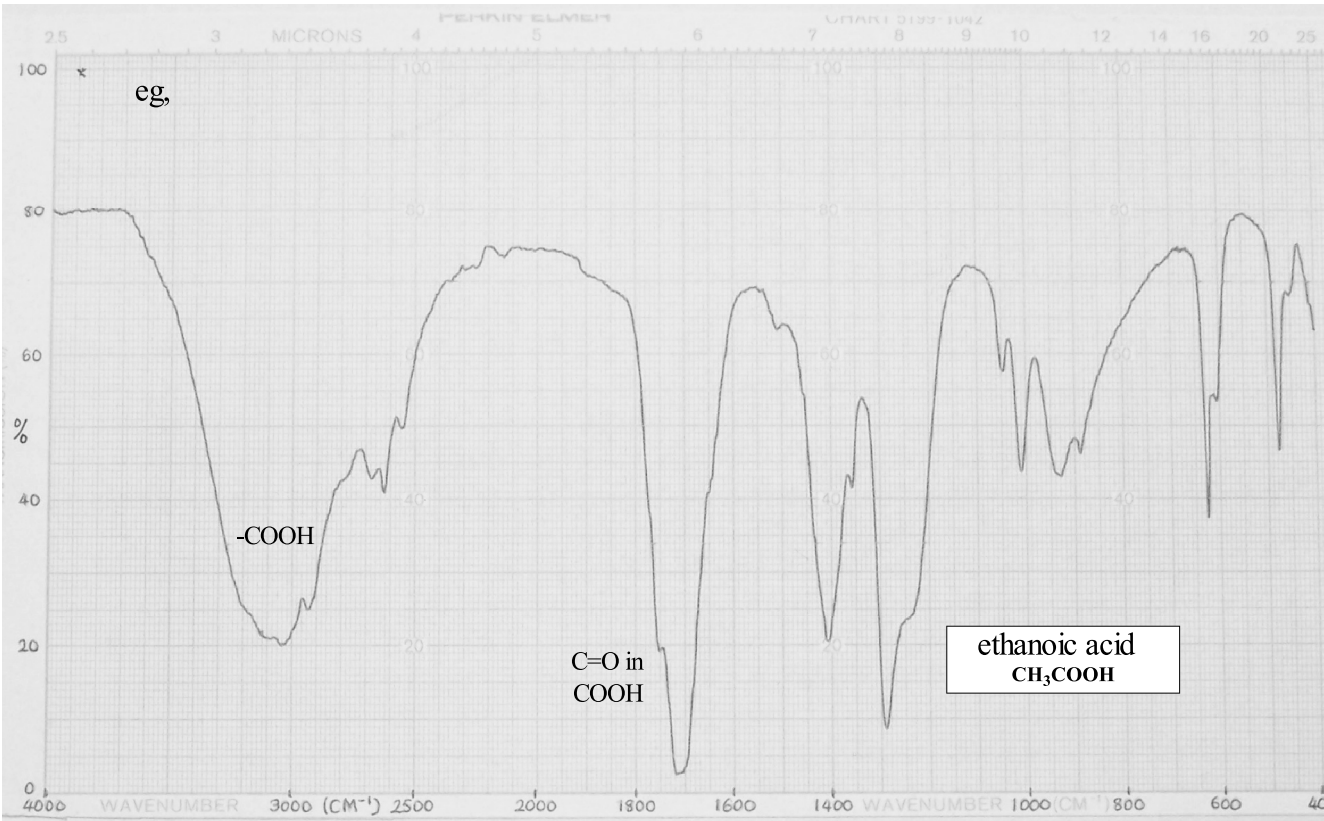
In the laboratory they are made by oxidising alcohols or aldehydes. They can also be made by hydrolysing nitriles. (see the carbonyl section, in this topic, for more details)

Industrial methods depend on which acid is required. Ethanoic acid, propanoic acid and butanoic acid can be manufactured together by oxidation of a mixture of alkanes (e.g., alkanes containing 4 to 6 carbon atoms). They are separated by fractional distillation.



## Infra-red spectroscopy of Carboxylic Acids

The carboxyl group generally gives intense very broad absorption centred around  $3000\text{ cm}^{-1}$ . The carbonyl component of the carboxyl group absorbs strongly in the region of  $1700\text{ cm}^{-1}$  and the peak is generally broad.



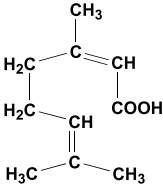
## Carboxylic Acids in Nature

eg,

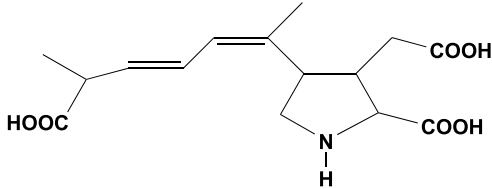
HCOOH - methanoic acid, present in the glandular fluid produced by some species of ants



butanoic acid - has a farmyard odour. It is present in animal excrements and is responsible for the smell of rancid butter.

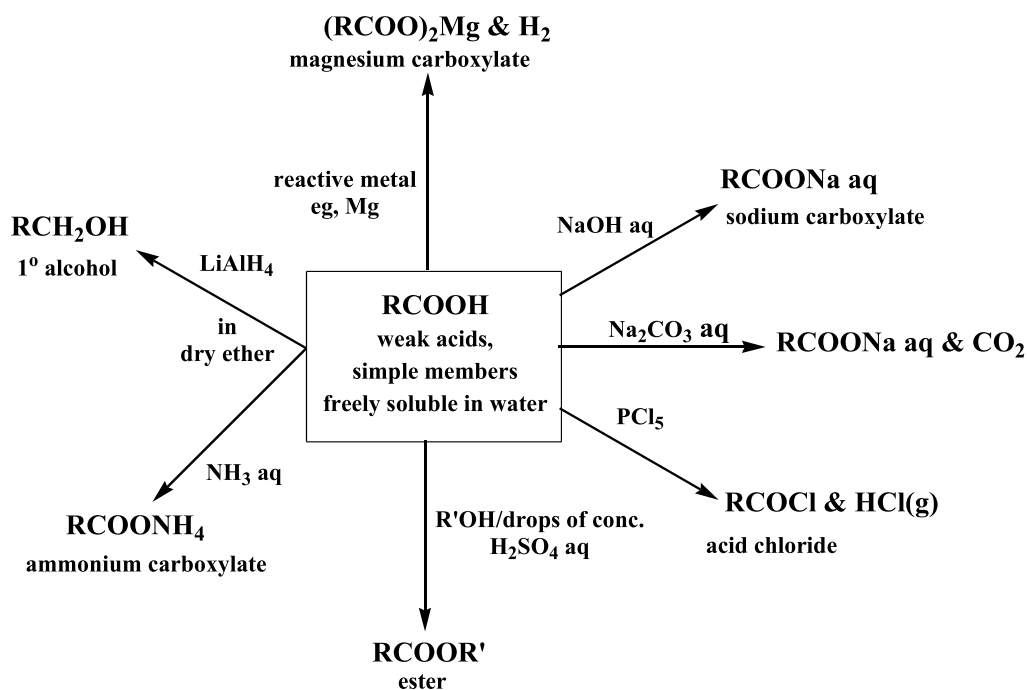
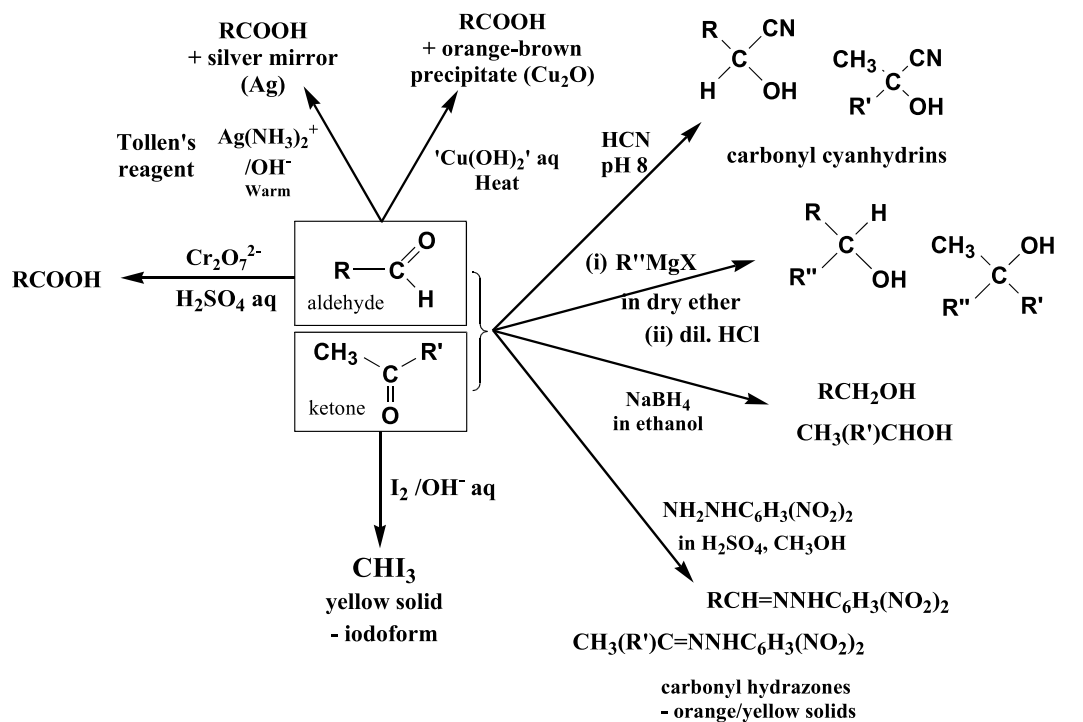


nerolic acid -  
along with other chemicals  
this is produced & released  
by bees



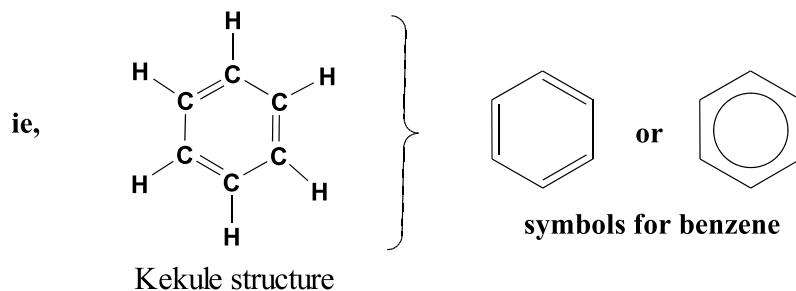
domoic acid -  
a neurotoxic detected in Japanese seaweed and in some  
shellfish

## Summaries:



## Arenes

Arenes are aromatic hydrocarbons; benzene is the simplest. It has a cyclic structure in which the carbon atoms are bonded to form a hexagonal ring. One hydrogen atom is attached to each carbon atom.

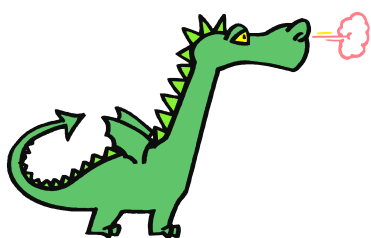


Have a look at: <http://en.wikipedia.org/wiki/Kekule>  
[http://www.rsc.org/chemsoc/timeline/pages/1864\\_benzene.html](http://www.rsc.org/chemsoc/timeline/pages/1864_benzene.html)

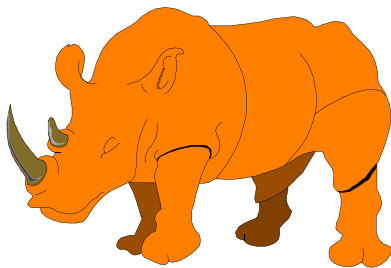
Each double bond consists of a sigma and pi bond.

The benzene structure is an example of a *resonance hybrid*. This is a general term used to refer to chemical structures which are not satisfactorily represented by a single structural formula and which, like benzene, show a marked degree of stability.

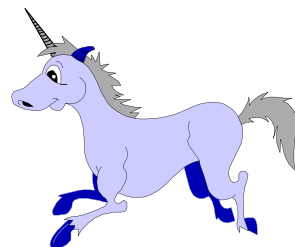
In attempting to explain the idea of a *resonance hybrid* D. J. Robinson has made the analogy between the resonance hybrid and a rhinoceros! He asks us to imagine that we are **not** familiar with the appearance of a rhinoceros and suggests that someone describing the creature may liken it to something between a unicorn and a dragon. The latter are mythical creatures and are unlikely to have existed, or exist. The rhinoceros on the other hand is a fact and yet has some of the characteristics of both the mythical unicorn and dragon. Similarly with the resonance hybrid; the hybrid exists and is the most favourable form of the molecule, exhibiting the characteristics of the other possible, but less favourable, structures (ie, canonical forms).



I'm sure I existed -  
didn't I?



I definitely exist!  
(OK I'm a funny colour but so what!?!)



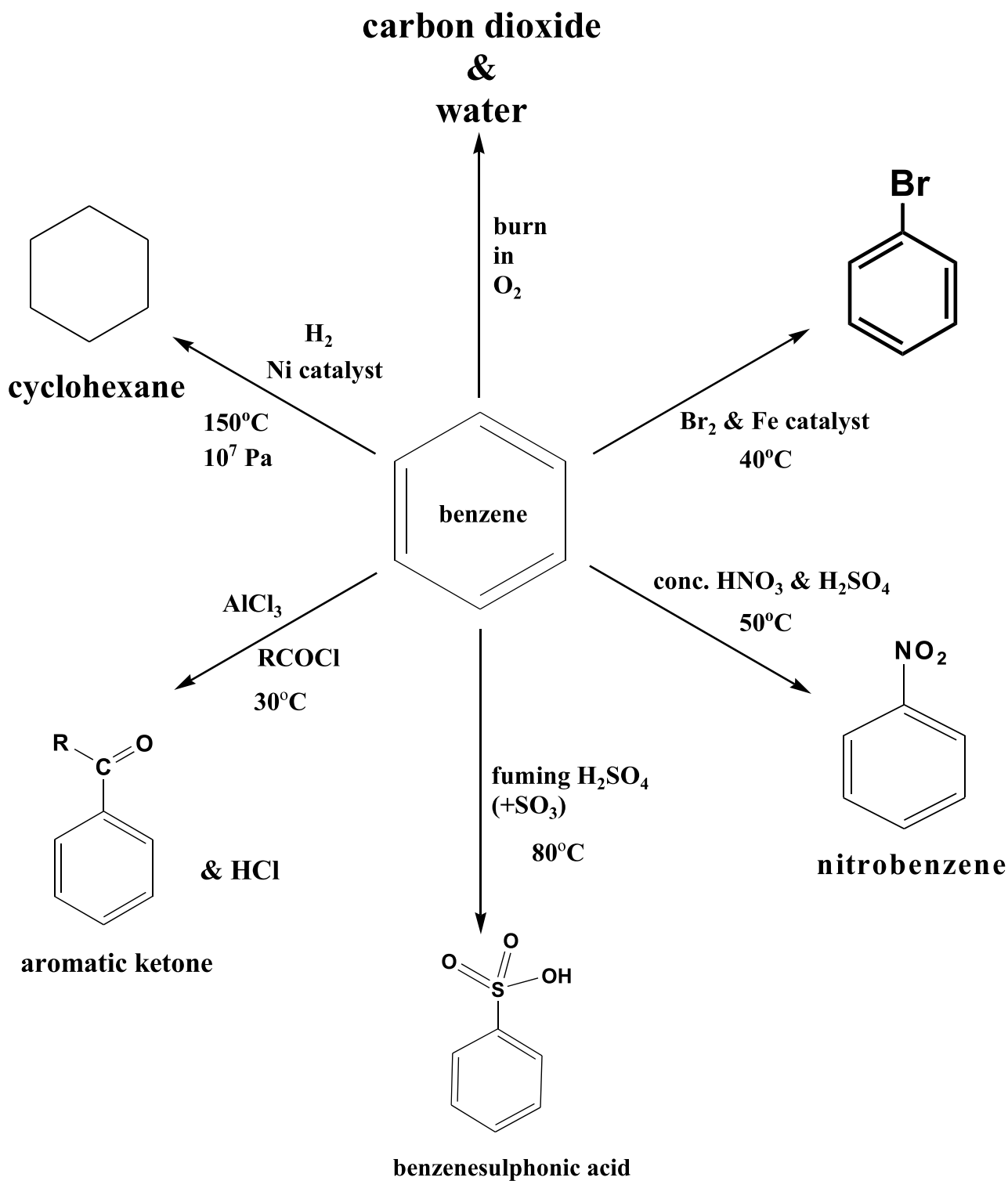
Come on now! Surely I exist?  
(In someone's imagination)

Chemists are generally agreed that in the benzene resonance hybrid the  $\pi$  electrons do not occupy fixed positions between the carbon atoms but are delocalised over the ring structure to provide annular clouds of electrons above and below the ring. The symbol above (far right) is often used to denote this.

## Organic Chemistry III

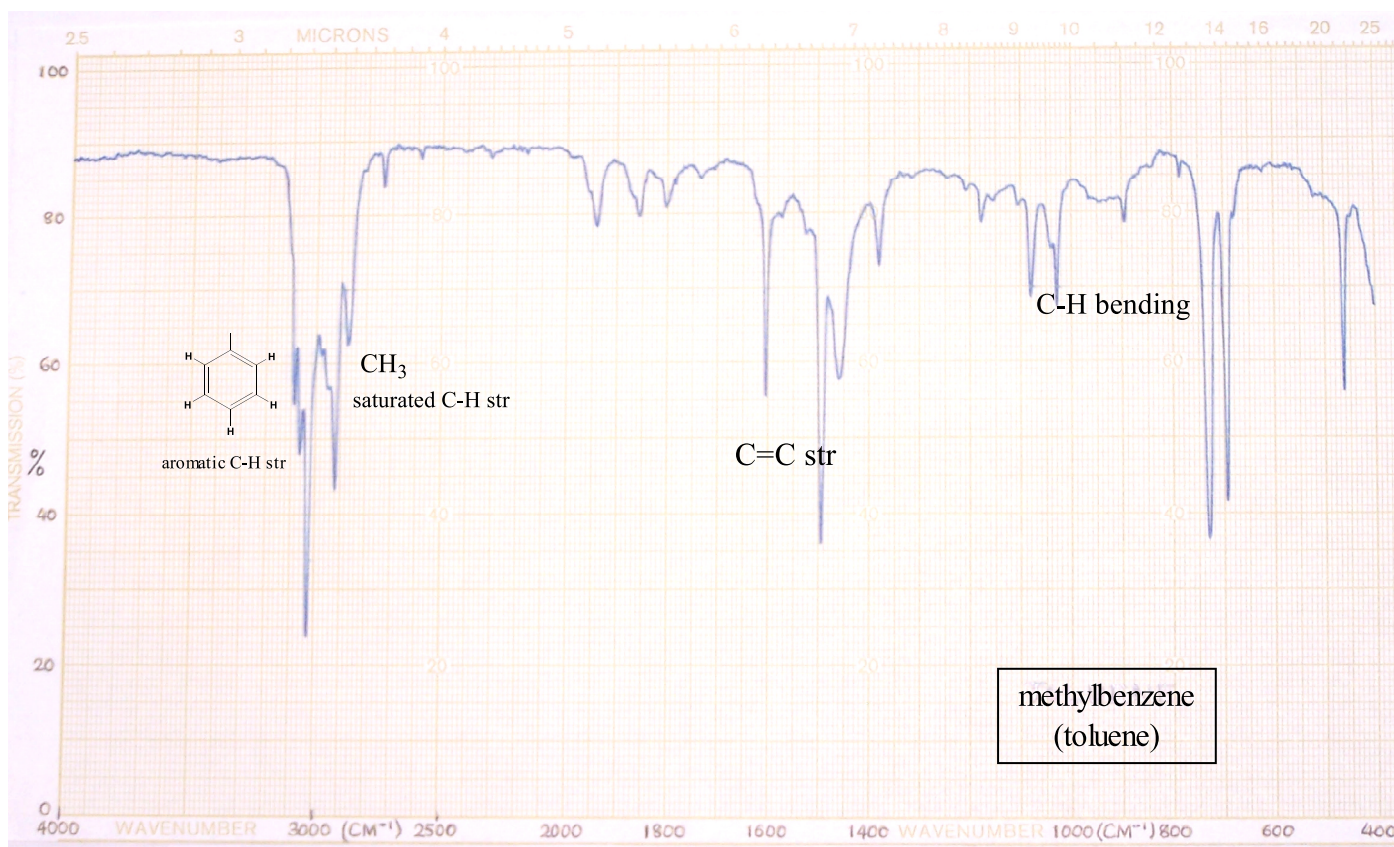
Benzene is a toxic, colourless, pleasant smelling liquid. It is insoluble in water, boils at  $80^{\circ}\text{C}$  and melts at  $6^{\circ}\text{C}$ .

Its typical reactions are *electrophilic substitution* although it does show some addition reactions.

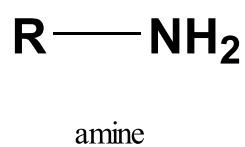
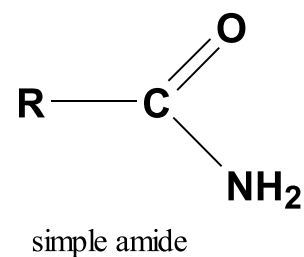
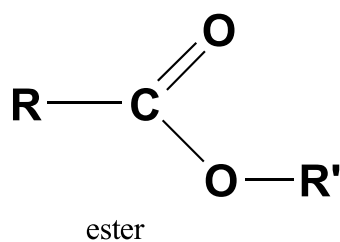
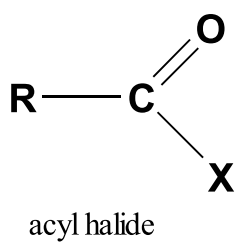




## The Infra-red Spectrum of Methylbenzene

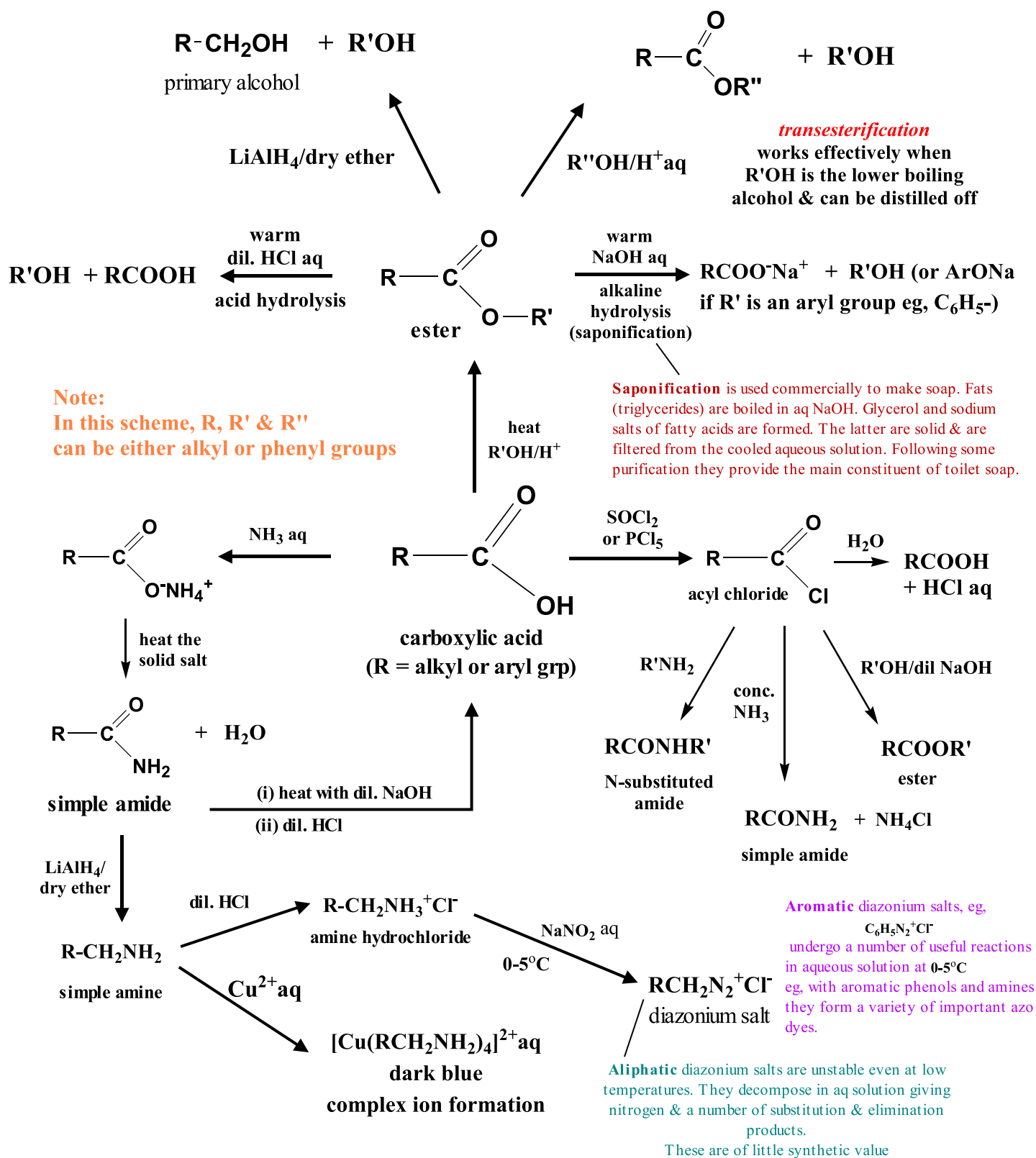


## Acyl Halides, Esters, Amines and Amides



R, R' = alkyl or aryl group, X = halogen

## Some general reactions:





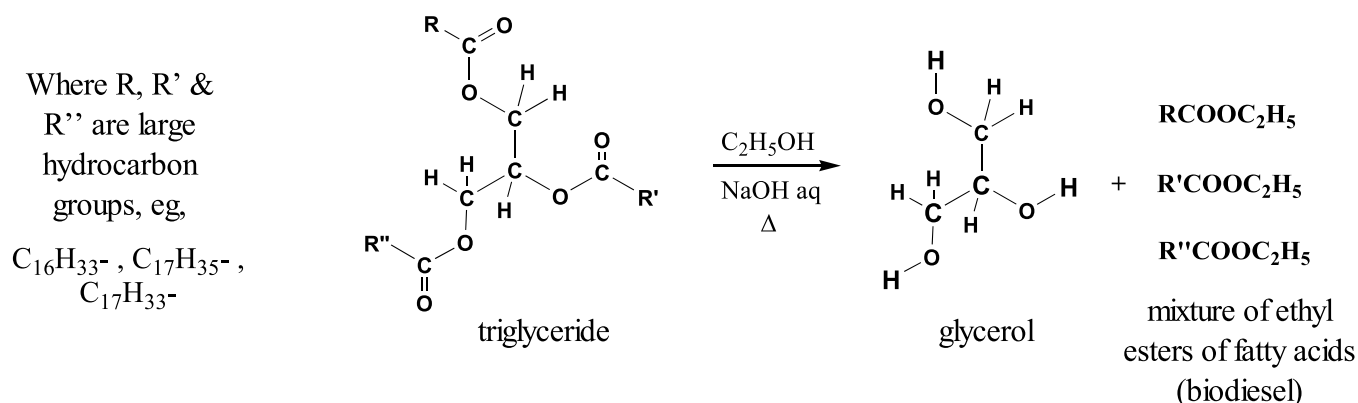
## Commercial Applications of Transesterification

### Biodiesel

Biodiesel is an engine fuel made from vegetable or animal fats. It is an alternative to diesel obtained from crude oil.

Virgin &/or waste vegetable and animal fats are transesterified by heating with sodium hydroxide dissolved in alcohol (ethanol or methanol). During this process the triglycerides, which constitute the fats, are converted to glycerol and ethyl (or methyl) esters of fatty acids (biodiesel).

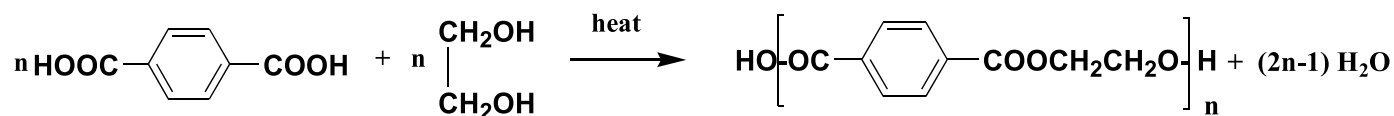
ie,



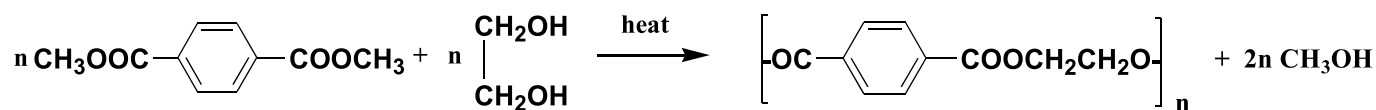
**Note:** Biodiesel, bioethanol, biobutanol and wood are examples of *carbon neutral* substances. When used as fuels they release carbon dioxide into the atmosphere but this is balanced by the carbon dioxide absorbed from the atmosphere by the plants used to produce them! We sometimes say they have a *zero carbon footprint*!

### Polyester

Terylene is an important example of a polyester. It is used to make plastic film and fibre for clothes. Terylene fibre is usually mixed with cotton fibre to improve wear and appearance. It can be synthesised by reacting benzene-1,4-dicarboxylic acid (terephthalic acid) with ethane-1,2-diol.



In practice, the dimethyl ester of terephthalic acid is used and methanol is the small molecule eliminated.



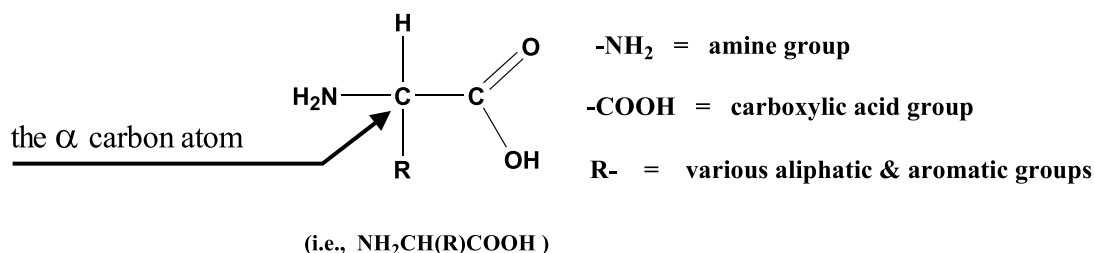
This reaction not only provides an example of transesterification it is also an example of *condensation polymerisation*, ie, polymerisation in which a small molecular mass product is also formed (in this case methanol).

## Proteins & Amino-acids

Proteins, like carbohydrates, are essential components of all living material. They are found in cells of both plants and animals. Although protein molecules come in all shapes and sizes, they all have a number of things in common. They all contain the element nitrogen, in addition to carbon, hydrogen and oxygen (and in some cases sulphur), and they all have molecular masses in excess of 10 000.

In some respects protein molecules are like nylon molecules. Both have high molecular masses and both contain the amide link (-NHCO-). Protein molecules differ from nylon molecules in that they are generally more complex in terms of structure. They have characteristic and complex shapes and they are built from small chemical units called  $\alpha$ -**amino acids**. A protein molecule may be constructed from a number of different  $\alpha$ -amino acids.

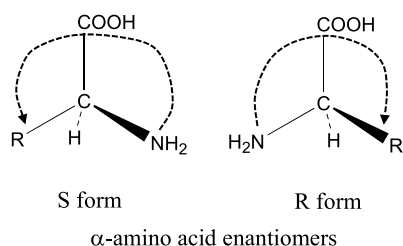
$\alpha$ -Amino acids have the general formula shown below.



Amino acids with this general structure are referred to as alpha ( $\alpha$ ) amino acids because the amine group is attached to the carbon atom next to ( $\alpha$  to) the carboxyl carbon.

Examples of naturally occurring  $\alpha$ -amino acids.

Since the  $\alpha$ -amino acids are chiral they exist in (S) and (R) forms.

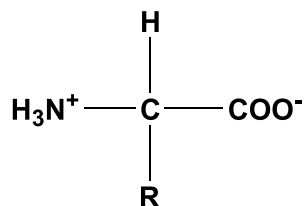


Enantiomers with the S configuration are found in nature.

Group R	Amino Acid Name
H-	glycine (aminoethanoic acid)
CH <sub>3</sub> -	alanine
CH <sub>3</sub> CH(OH)-	threonine
	valine
HOOC-CH <sub>2</sub> -	aspartic
	phenylalanine
NH <sub>2</sub> (CH <sub>2</sub> ) <sub>4</sub> -	lysine
	tyrosine

$\alpha$ -Amino acids melt at temperatures above 200°C, they are white crystalline solids and are soluble in water (some, however, are much more soluble than others). These properties suggest that amino acids are, in fact, **ionic** compounds.

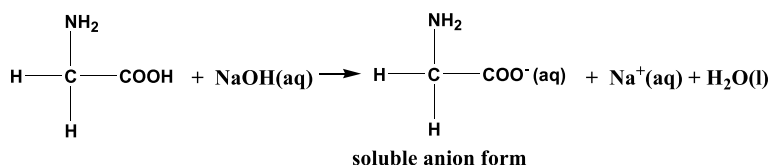
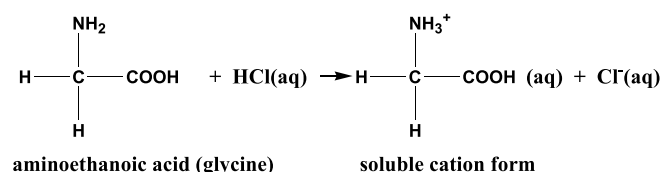
They are better represented by the following general formula:



amino acid dipolar ion structure

For the purpose of writing simple chemical equations, it is quite acceptable to use the simplified general formula given previously (i.e.,  $\text{NH}_2\text{CH(R)COOH}$ ).

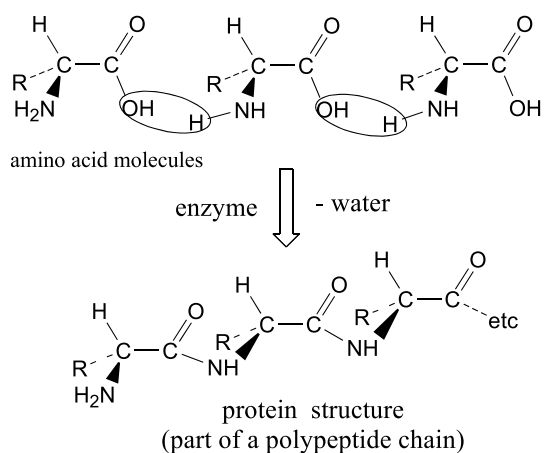
$\alpha$ -Amino acids are **amphoteric**. They react with both acids and alkalis.



Due to their amphoteric nature, amino acids exhibit buffer action in aqueous solution. They can take up either hydrogen ion or hydroxide ion. The resulting solution, however, will have a different pH to the original solution of the amino acid and therefore pH is controlled but not maintained at the original value.

In animal and plant cells amino acid molecules are combined by the catalytic action of certain enzymes, to give protein molecules.

The process of protein synthesis can be reversed by boiling the protein with dilute hydrochloric acid. This produces a mixture of free amino acids which can be analysed by chromatography. On the basis of this chromatography and the results of more detailed analyses it is often possible to determine the number and type of amino acids making up the original protein molecule.





# Acid-Base Equilibria

## Equilibria in Aqueous solutions

Many laboratory and industrial reactions and all biological reactions take place in aqueous solutions. It is important, therefore, to understand the kind of equilibria which can occur in *water*.

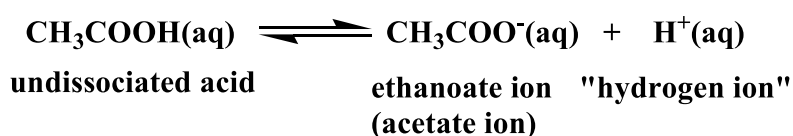
A water soluble substance (the *solute*) is one which breaks up into smaller and smaller fragments ultimately yielding molecular particles which become dispersed amongst the water molecules to give a clear solution.

## Dissociation

In some cases, a dissolved *molecular* substance breaks up further to give ions; it is said to **dissociate**. In this case an equilibrium is established, in the solution, between these ions and the undissociated solute molecules.

eg,

The carboxylic acid, ethanoic acid (acetic acid), is freely soluble in water and ***partially*** dissociates:



Ethanoic acid is an example of a ***weak*** acid and the extent of the dissociation is expressed by the equilibrium constant (K).

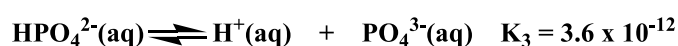
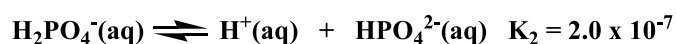
$$K = \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]}$$

For ethanoic acid  $K = 1.8 \times 10^{-5}$  at  $25^\circ \text{C}$

Some acids have more than one dissociation constant.

e.g.,

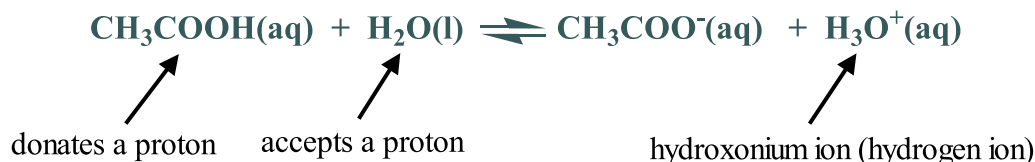
The tribasic acid, phosphoric acid:



## Acid-Base Equilibria

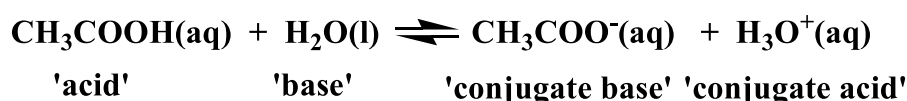
### Lowry-Bronsted (1923)

Strictly, the equilibrium should show the participation of the water (the solvent).  
i.e.,



According to the **Lowry-Bronsted** definition of acids and bases;  
 an acid = proton donor  
 a base = proton acceptor.

In the above equilibrium, the water is acting as a base since it accepts a proton from the acid.  
 Therefore:



$\text{CH}_3\text{COOH}$  &  $\text{CH}_3\text{COO}^-$  are a 'conjugate acid-base pair' as are  $\text{H}_2\text{O}$  &  $\text{H}_3\text{O}^+$  (the word *conjugate* means joined in pairs)

The new equilibrium expression showing the involvement of water is:

$$K' = \frac{[\text{CH}_3\text{COO}^-][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{COOH}][\text{H}_2\text{O}]}$$

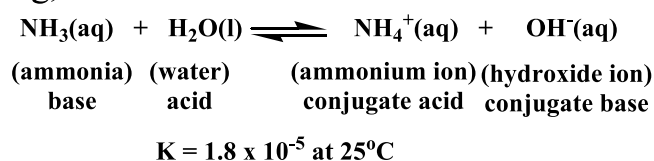
However, if the solution is dilute, the term  $[\text{H}_2\text{O}]$  will be large and more or less constant. It can be combined with  $K'$  to give  $K$ .

We then have, 
$$K = \frac{[\text{CH}_3\text{COO}^-][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{COOH}]}$$

The term,  $[\text{H}_3\text{O}^+] = [\text{H}^+]$  as in the previous expression.

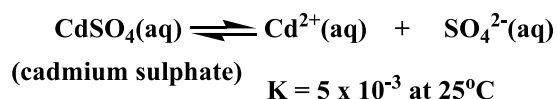
Weak bases are treated similarly.

e.g,



Some salts are partially dissociated in aqueous solution.

e.g,



## Calculating the concentrations of solute species in an equilibrium mixture

What is the concentration of all solute species in a solution labelled 1.00M ethanoic acid?  
( $K = 1.8 \times 10^{-5}$  at  $25^\circ\text{C}$ )

The equilibrium may be represented:



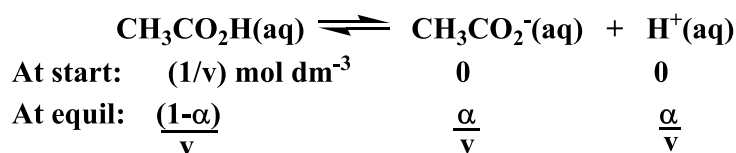
### Deriving a general expression

Suppose we have a solution containing 1 mole of acid in  $v \text{ dm}^3$ .

Then, the initial concentration of acid =  $(1/v) \text{ mol dm}^{-3}$ .

At equilibrium some of this acid will have dissociated. Let the amount dissociated be represented  $\alpha$  (the *degree of dissociation*).

Then,



Since, 
$$K = \frac{[\text{CH}_3\text{CO}_2^-] [\text{H}^+]}{[\text{CH}_3\text{CO}_2\text{H}]}$$

$$K = \frac{(\alpha/v) (\alpha/v)}{(1-\alpha)/v} = \frac{\alpha^2}{v^2} \times \frac{v}{1-\alpha} = \frac{\alpha^2}{v(1-\alpha)}$$

$$K = \frac{\alpha^2}{v(1-\alpha)}$$

This is known  
as **Ostwald's**  
**dilution law**

For a *dilute* solution of a weak acid the term  $(1-\alpha)$  can be ignored since it is close to unity.

Then,

$$K = \frac{\alpha^2}{v}$$

## Acid-Base Equilibria

In this particular example,  $v = 1 \text{ dm}^3$  (the volume containing 1 mole of acid).  
Therefore,

$$K = \frac{\alpha^2}{1} = 1.8 \times 10^{-5}$$

$$\& \alpha = \sqrt{1.8 \times 10^{-5}} = 4.2 \times 10^{-3} \text{ mol}$$

$$[\text{CH}_3\text{COOH}] = 1 - \alpha = 1 - 0.0042 = 0.9958 \text{ mol dm}^{-3}$$

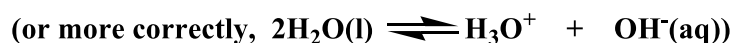
$$[\text{CH}_3\text{COO}^-] = \alpha = 0.0042 \text{ mol dm}^{-3}$$

$$[\text{H}^+] = \alpha = 0.0042 \text{ mol dm}^{-3}$$

$$\text{And \% dissociation of the acid} = \frac{\alpha/v}{1/v} \times 100 = 0.42\%$$

## Dissociation of Water

Water is a very weak electrolyte.



$$\text{Therefore, } K = \frac{[\text{H}^+][\text{OH}^-]}{[\text{H}_2\text{O}]}$$

Since  $[\text{H}^+]$  and  $[\text{OH}^-]$  are very very small compared with  $[\text{H}_2\text{O}]$ ,  $[\text{H}_2\text{O}]$  is constant and can be incorporated into the value of  $K$ .

Then,

$$K_{\text{water}} = [\text{H}^+][\text{OH}^-] = K_w$$

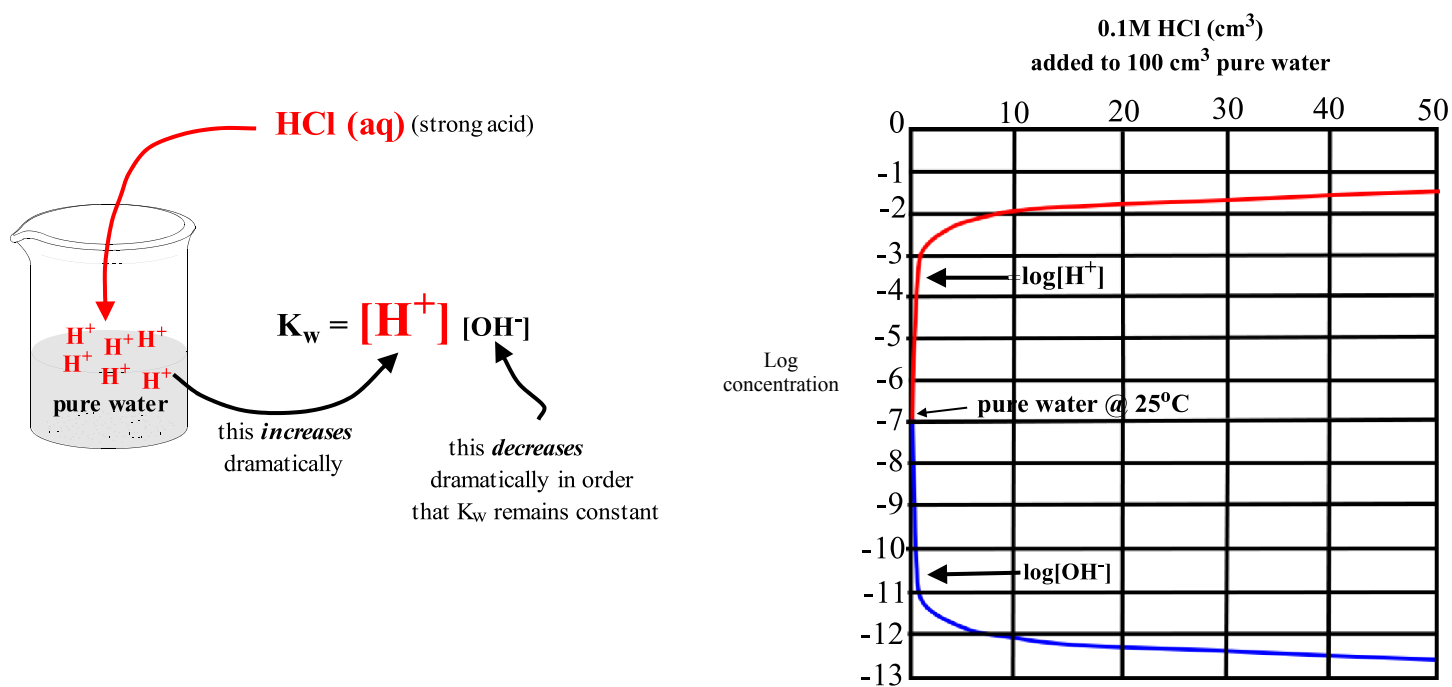
This is known as the *ionic product of water*. At  $25^\circ\text{C}$  it has a value of  $1 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$ .

$$\text{Then, } [\text{H}^+] = [\text{OH}^-] = \sqrt{1 \times 10^{-14}} = 1 \times 10^{-7} \text{ mol dm}^{-3}$$

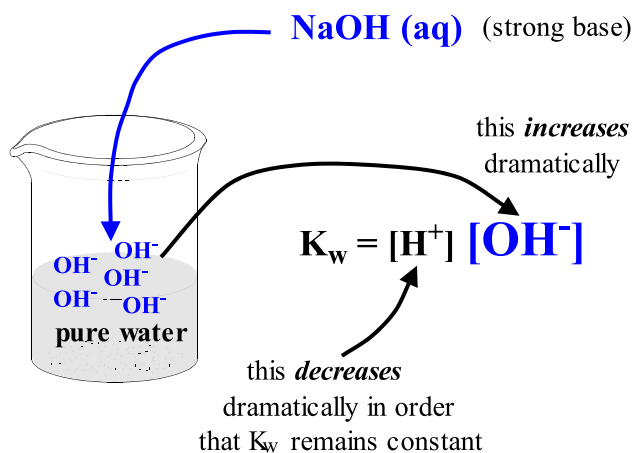
In pure water the ratio of water molecules to hydrogen ions is 554 million : 1 !

## Acid-Base Equilibria

**What happens if we add strong acid or base to pure water?**



Similarly when strong base is added to water





# pH

This is another way of expressing hydrogen ion concentration. It avoids the rather unwieldy numbers which are obtained when concentrations are expressed in mol per cubic decimetre.

$$\text{pH} = -\log_{10}[\text{H}^+]$$

**Note:** this relationship only applies accurately at low concentrations ( $< 0.1\text{M}$ ).

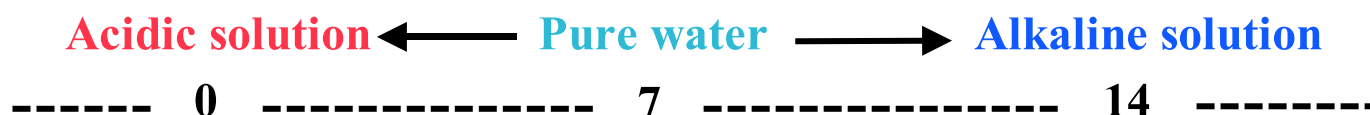
$$\text{or } \text{pH} = \log_{10} \frac{1}{[\text{H}^+]}$$

If accurate pH values are required for aqueous solutions they must be measured using a calibrated pH meter.

In pure water,  $[\text{H}^+] = 1 \times 10^{-7} \text{ mol dm}^{-3}$

Therefore,  $\text{pH} = -\log_{10}[\text{H}^+] = -\log 10^{-7} = 7.00$

### pH scale:



What is the pH of 0.1M HCl?

$$\text{pH} = -\log_{10}[\text{H}^+] = -\log 10^{-1} = 1.00$$

What is the hydrogen ion concentration of a solution of  $\text{pH} = 12.35$ ?

$$\text{pH} = -\log_{10}[\text{H}^+] = 12.35$$

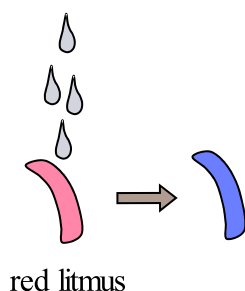
therefore,

$$\log[\text{H}^+] = -12.35$$

$$[\text{H}^+] = \text{antilog}(-12.35) = 4.467 \times 10^{-13} \text{ mol dm}^{-3}$$

## Acid-Base Equilibria

### Alkaline Solutions



These have pH values above 7.

eg,

What is the pH of 0.1M NaOH?

$$K_w = [H^+] [OH^-] = 1 \times 10^{-14}$$

$$\text{so } [H^+], \text{ in } 0.1M \text{ NaOH, } = \frac{1 \times 10^{-14}}{0.1} = 10^{-13}M$$

$$\text{Then, } pH = -\log 10^{-13} = 13.00$$

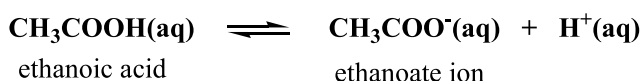
### Buffer Solution

*This is a solution which is capable of maintaining its pH more or less constant even when small amounts of strong acid or base are added to it.*

Human blood is a good example. This has a pH close to 7.4 which remains constant in spite of numerous acid-base reactions taking place in the cells. There is only a difference of 0.02 pH units between arterial and venous blood.

A much simpler example is provided by a solution containing equimolar amounts of ethanoic acid and sodium ethanoate. This mixture can maintain a pH of about 4.7 even when small amounts of strong acid or base are added to it.

The following equilibrium represents the mixture:



$$K_a = \frac{[H^+] [CH_3COO^-]}{[CH_3COOH]}$$

$$[H^+] = K_a \frac{[CH_3COOH]}{[CH_3COO^-]}$$

Taking logs of each side,

$$-\log[H^+] = -\log K_a - \log \frac{[CH_3COOH]}{[CH_3COO^-]}$$

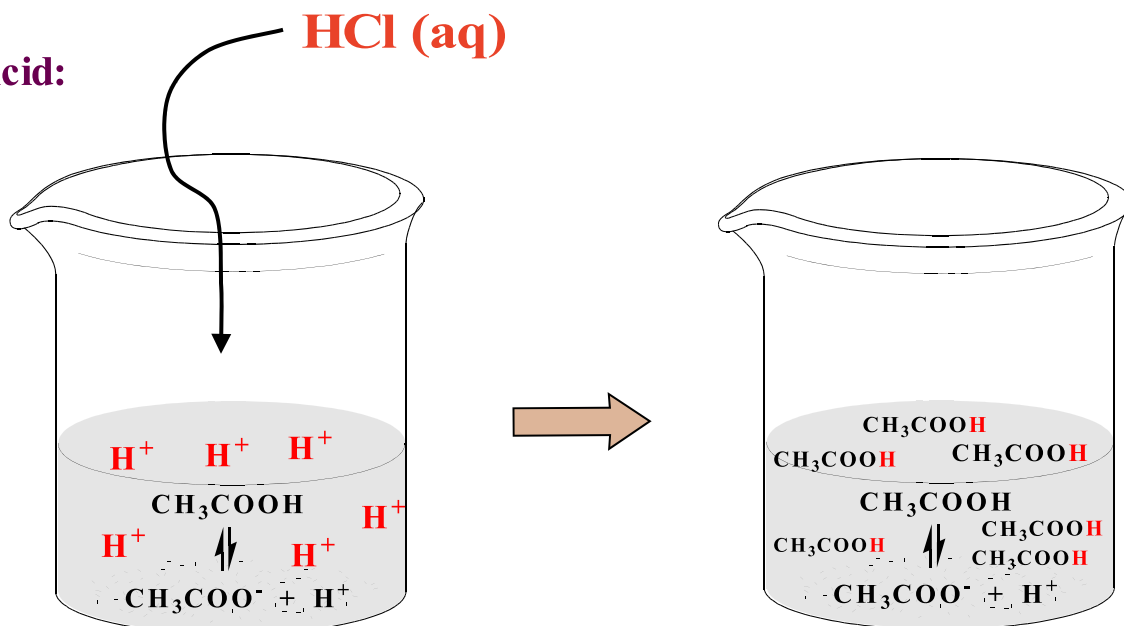
$$\text{ie, } pH = pK_a + \log \frac{[CH_3COO^-]}{[CH_3COOH]}$$

This equation, known as the **Henderson-Hasselbalch** equation, enables the pH of the solution to be calculated for varying concentrations of acid and its salt.

Notice that when, [ethanoic acid] = [ethanoate ion], pH is given by the pK<sub>a</sub> value (4.74). Under these conditions, adding small amounts of strong acid or base does not significantly alter the value of the last term in the equation and the pH of the mixture remains close to 4.74. We say the mixture is a 4.74 buffer. We also say the **buffer region** is centred about the pK of the acid.

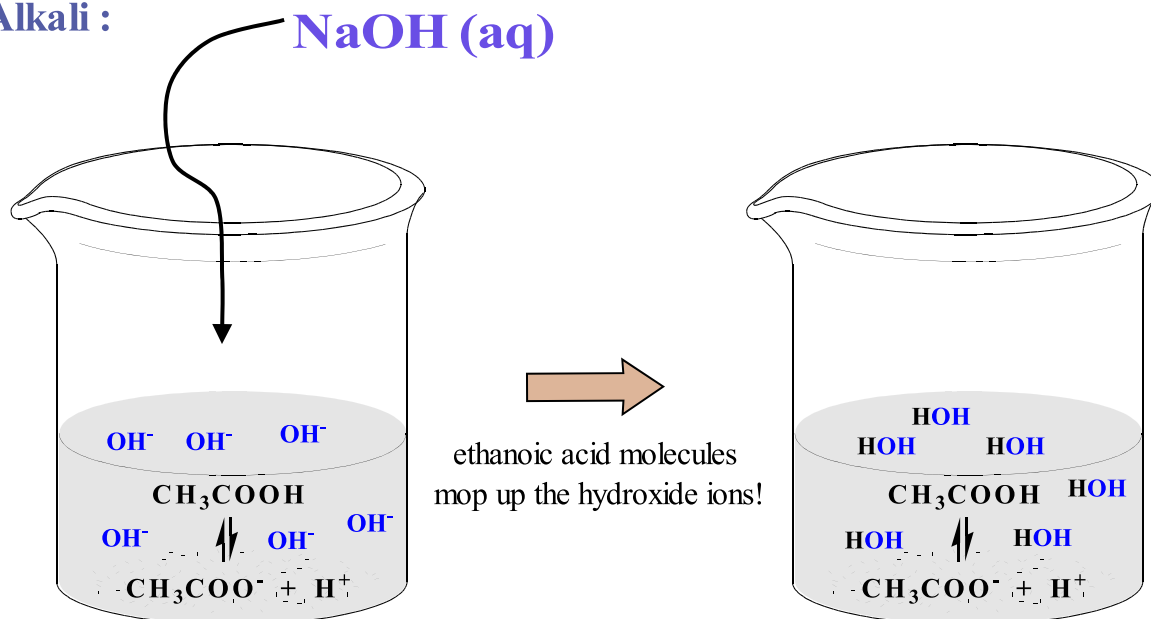
## Buffer action: How it works.

### Adding Acid:



The hydrogen ion concentration immediately rises as the strong acid is added, however, the high number of ethanoate ions rapidly combine with the hydrogen ions forming undissociated ethanoic acid molecules. The ethanoate ions mop up the hydrogen ions! Equilibrium is re-established and in this way the original pH of the solution (ie, 4.7) is maintained.

### Adding Alkali :



## Acid-Base Equilibria

Besides *acid* buffer solutions there are *base* buffer solutions. These are solutions containing a weak base and a salt of the base.

eg,  $\text{NH}_3(\text{aq})/\text{NH}_4\text{Cl}(\text{aq})$



If acid is added to an aqueous solution containing ammonia and ammonium chloride, the hydrogen ions combine with hydroxide ions to give water and the equilibrium moves to the right. The pH of the solution stays about constant.

There are as many buffers as there are weak acids and bases.

## Acid-Base Titrations

When we carry out an acid-base titration such as the titration of dilute hydrochloric acid against dilute sodium hydroxide the following equilibrium is being affected



and at each step in the titration  $K_w$  must be satisfied, ie,  $K_w = [\text{H}^+][\text{OH}^-] = 1 \times 10^{-14}$  at  $25^\circ\text{C}$

Just to illustrate this suppose we have a litre of 0.01M HCl and we wish to neutralise it by adding solid NaOH a little at a time (we would **not** normally use *solid* sodium hydroxide but in this example it is convenient since it makes the arithmetic easier!).

**At the start:**  $[\text{H}^+] = 0.010 \text{ mol dm}^{-3}$ ,  $[\text{OH}^-] = 1.0 \times 10^{-12} \text{ mol dm}^{-3}$  &  $\text{pH} = 2.00$

**At the half way stage, when 0.005 mol of NaOH has been added:**

$[\text{H}^+] = 0.005 \text{ mol dm}^{-3}$ ,  $[\text{OH}^-] = 2.0 \times 10^{-12} \text{ mol dm}^{-3}$  &  $\text{pH} = 2.30$

**At the neutralisation point (end point) 0.010 mol of NaOH has been added:**

$[\text{H}^+] = 1 \times 10^{-7} \text{ mol dm}^{-3}$ ,  $[\text{OH}^-] = 1 \times 10^{-7} \text{ mol dm}^{-3}$  &  $\text{pH} = 7.00$

At each stage  $K_w$  remains constant at  $1 \times 10^{-14}$

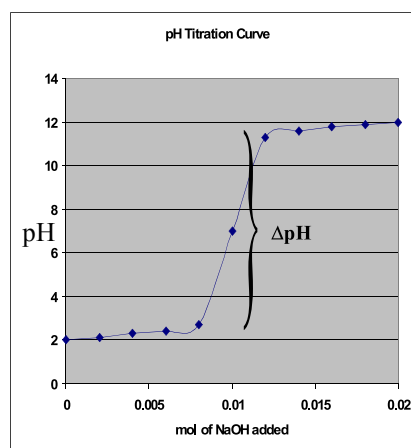
## Acid-Base Equilibria

If, in an acid-base titration, we plot pH against amount of base added (to a fixed amount of acid) the result is an **acid-base titration curve**.

eg,

### (i) Strong acid versus strong base eg, 0.01M HCl versus dil. NaOH

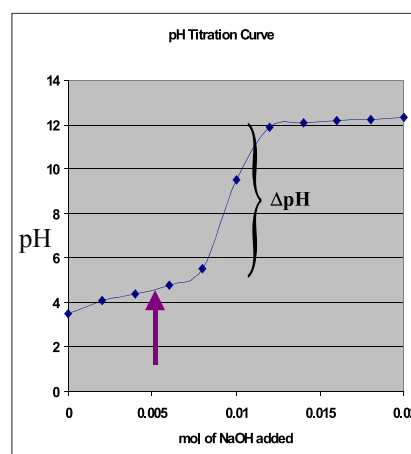
Notice how the pH changes rapidly in the region of the end point. Also, notice the large  $\Delta\text{pH}$  value ie, approx. 10 pH units. This is characteristic for a strong acid-strong base titration.



### (ii) Weak acid versus strong base eg, 0.01M ethanoic acid versus dil. NaOH

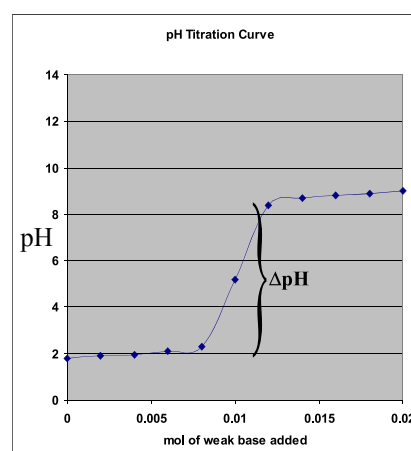
Notice once again pH changes rapidly at the end point. This time however,  $\Delta\text{pH}$  is approximately 6 units. It is smaller than for a strong acid against a strong base. At the half way stage in the titration  $\text{pH} = \text{pK}_a$  since at this point  $[\text{acid}] = [\text{carboxylate ion}]$  (ref to Henderson-Hasselbach equation).

A titration curve like this provides a convenient method of finding  $K_a$  for a weak acid.  $\uparrow$



### (iii) Strong acid versus weak base eg, 0.01M HCl versus ammonia solution

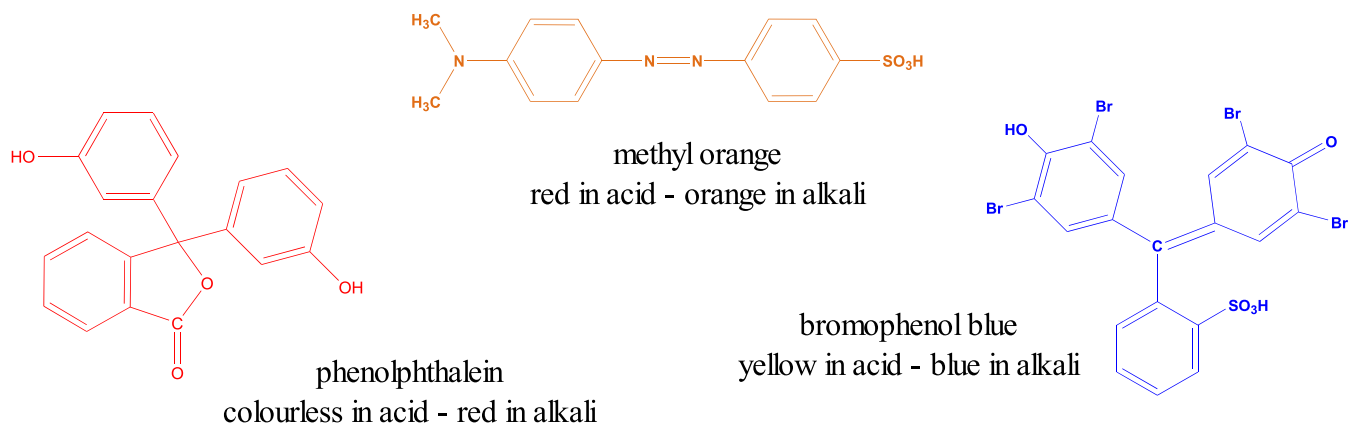
Notice again a rapid change in pH at the end point.  $\Delta\text{pH}$  is again only about 6 units.



## Indicators

Many coloured organic substances, such as dyes, are sensitive to hydrogen ion concentration and may be used to detect the end-point in a titration. Since these substances indicate the end-point they are called *indicators*.

Some examples:



Many indicators are weak acids and may be represented by the symbol, HIn. In aqueous solution dissociation occurs:



If HIn(aq) and In<sup>-</sup>(aq) are different colours the solution will undergo a colour change over a narrow and characteristic pH range.

eg,            methyl orange: red to orange, **pH range** 3.1 to 4.4  
                  phenolphthalein: colourless to red, **pH range** 8.3 to 10.0  
                  bromophenol blue: yellow to blue, **pH range** 3.0 to 4.6

In the case of phenolphthalein in aqueous solution, you would observe the solution to be colourless below pH 8.3 and you would observe the **full** red colour at pH 10 & above. In between these pH values the colour would be lighter shades of red (or pink).

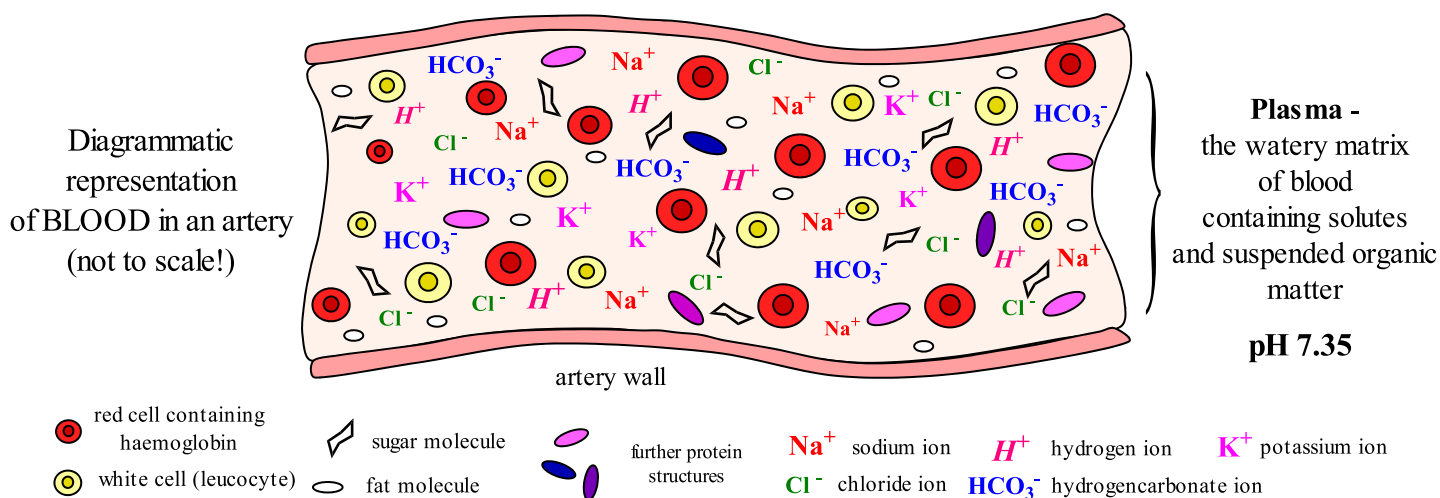
When [HIn(aq)] = [In<sup>-</sup>(aq)] then pH = pK<sub>HIn</sub>. For phenolphthalein this value is 9.2 which is approximately the mid point of the pH range. The value 9.2 is referred to as the **pK<sub>a</sub> of the indicator**.

The pK<sub>a</sub> of methyl orange is 3.7 and for bromophenol blue it is 4.0.

When choosing an indicator for an acid-base titration make sure its pK<sub>a</sub> value is towards the centre of ΔpH for the titration (see titration curves on previous page). For example, looking at the titration curve for a **weak acid** versus **strong base** where the centre of ΔpH is about pH 9, methyl orange and bromophenol blue would be unsuitable. Phenolphthalein would be fine!

## Buffer action in Blood

Blood is a complex aqueous mixture of molecular structures and ions:



Blood is required to transport oxygen & nutrients around the body and to remove waste products from the tissues. One of these waste products is **carbon dioxide** which is transported to and expired in the lungs. Over 85% of the carbon dioxide produced by the body tissues is conveyed to the lungs as **hydrogencarbonate ion** and about 90% of this is carried in the red blood cells. When the red cells reach the lungs  $\text{HCO}_3^-$  is combined with  $\text{H}^+$  to give carbon dioxide gas which is then expelled into the alveoli. This conversion of hydrogencarbonate ion to carbon dioxide occurs rapidly as haemoglobin releases hydrogen ion ([Bohr effect](#)) as it takes up oxygen in the lungs.

In order for these reactions to occur smoothly and efficiently the pH of the blood must be maintained close to **7.35**. Variations within  $\pm 0.05$  of this value are normal. Greater variations give rise for concern; a blood pH of 7.2, for example, would constitute a serious health risk!

A number of buffers act together maintaining the optimal pH value (7.35). **Haemoglobin** and other protein rich structures have numerous  $-\text{NH}_3^+$  and  $-\text{COO}^-$  groups on their surfaces which exchange with hydrogen and hydrogencarbonate ions and serve to control the concentrations of these ions in the plasma and blood cells. Additionally, and most important, is the buffer action of hydrogencarbonate itself. It forms an equilibrium mixture, in the blood, with dissolved carbon dioxide and hydrogen ion. This equilibrium lies to the left and is catalysed by **carbonic anhydrase** in the blood.

ie,



If the blood was to receive a surge of hydrogen ion, as a result of a diabetic problem, for example, hydrogencarbonate ion would mop up the hydrogen ion and the above equilibrium would move to the left (in favour of water and dissolved carbon dioxide). This excess of dissolved carbon dioxide would be reduced by increased breathing and expulsion of carbon dioxide gas via the lungs.

Following these adjustments the pH of the plasma would quickly return to 7.35.

## Acid-Base Equilibria

The following expressions relates to the hydrogencarbonate equilibrium in plasma:

$$K_a = \frac{[H^+(aq)][HCO_3^-(aq)]}{[CO_2(aq)]} \quad \text{Then,} \quad [H^+(aq)] = \frac{K_a [CO_2(aq)]}{[HCO_3^-(aq)]}$$

$$-\log [H^+(aq)] = -\log K_a + \log \frac{[HCO_3^-(aq)]}{[CO_2(aq)]}$$

$$pH = pK_a + \log \frac{[HCO_3^-(aq)]}{[CO_2(aq)]}$$

At 37°C (body temperature),  $pH = 6.1 + \log \frac{[HCO_3^-(aq)]}{[CO_2(aq)]}$       equ 1

In plasma, under normal conditions,

$[HCO_3^-(aq)] = 24 \times 10^{-3} \text{ mol dm}^{-3}$   
and  $[CO_2(aq)] = 1.2 \times 10^{-3} \text{ mol dm}^{-3}$

Then,

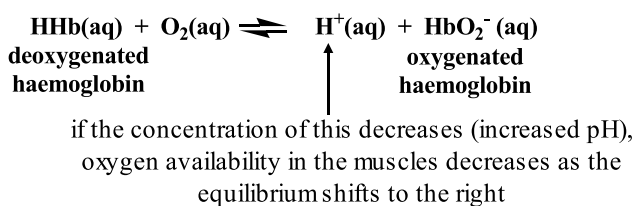
$$pH = 6.1 + \log \frac{24}{1.2} = 6.1 + 1.3 = 7.4$$

( If necessary,  $[CO_2(aq)]$  can be expressed as a gas pressure since  $[CO_2(aq)] = 0.03 p_{CO_2}$  where  $p_{CO_2}$  is the partial pressure of the gas in the alveolar air (this has a normal value of 5333 Pa , 40 mmHg)).

In sport we often hear of athletes going for acclimatization prior to competing in events at high altitude venues. The purpose of this is to get them used to competing in an atmosphere where the partial pressure of oxygen is less than what they are used to.

If you are suddenly exposed to a more rarified atmosphere (eg, as would be the case at, say, 3000m above sea level), the partial pressure of oxygen in your lungs would be reduced. Your reaction to this would be to breath more rapidly to try and get more oxygen! The effect of this would be to expire carbon dioxide at a faster rate and *reduce* dissolved carbon dioxide in your blood plasma. From equation 1, this would *increase* the pH of your blood. The knock on effect of this would be to reduce the availability of oxygen to the muscles and your athletic performance would be impaired. Clearly this would be bad news if you happened to be competing in a marathon; you would quickly collapse from oxygen starvation and fatigue.

The reason for reduced oxygen availability at the muscles, in this scenario, is as a result of the following equilibrium involving haemoglobin:





# Theme Fourteen

## Redox Equilibria

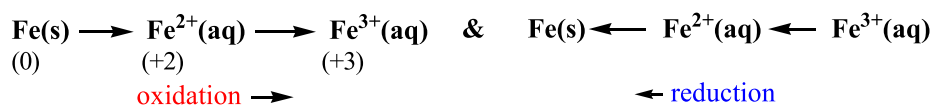
### Reduction-Oxidation (Redox) and Oxidation Number

You will need to refresh your memory on this subject.

Just to remind you, atoms are attributed oxidation numbers to indicate their oxidation state. The more positive the oxidation number the more oxidised the atom.

The opposite of oxidation is reduction. The more negative the oxidation number the more reduced the atom.

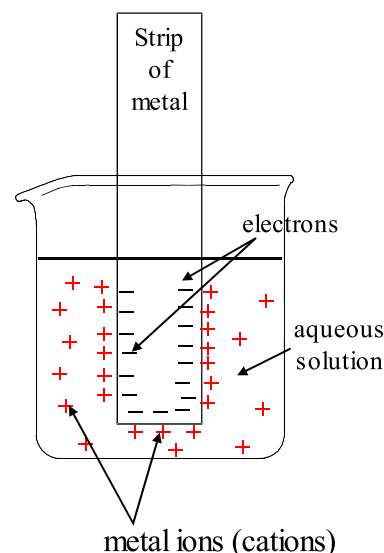
Eg, there are three oxidation states of iron, **iron Fe**, **iron(II) Fe<sup>2+</sup>** and **iron(III) Fe<sup>3+</sup>**. Iron (the metal) has the oxidation number **0**, iron(II) has the oxidation number **+2** and iron(III) the oxidation number **+3**. Iron (III) is the more oxidised state. Conversion of iron to iron(II) and iron(II) to iron(III) involves *oxidation*. Conversion of iron(III) to iron(II) and iron(II) to iron involves *reduction*.



### Electrode Potential (or, Redox Potential)

When a metal is placed in a solution of its ions it shows a *tendency* to dissolve. For metals other than those in group I, this process is not particularly dramatic. A strip of iron, for example, placed in a dilute solution of iron(II) sulphate changes its appearance only very slowly as the surface turns brownish and the metal *rusts*.

However, if we could see the surface metal atoms we would observe a flow of atoms from the surface to the solution and visa versa. The surface of the metal would acquire a small negative potential with respect to the surrounding solution as electrons accumulate on the metal surface. This small negative charge, relative to the surrounding solution, is referred to as the electrode potential or redox potential. It arises as a result of ionisation and hence oxidation, of the metal atoms at the metal/solution interface. After a while, an equilibrium is established between metal atoms at the surface and metal ions in solution.



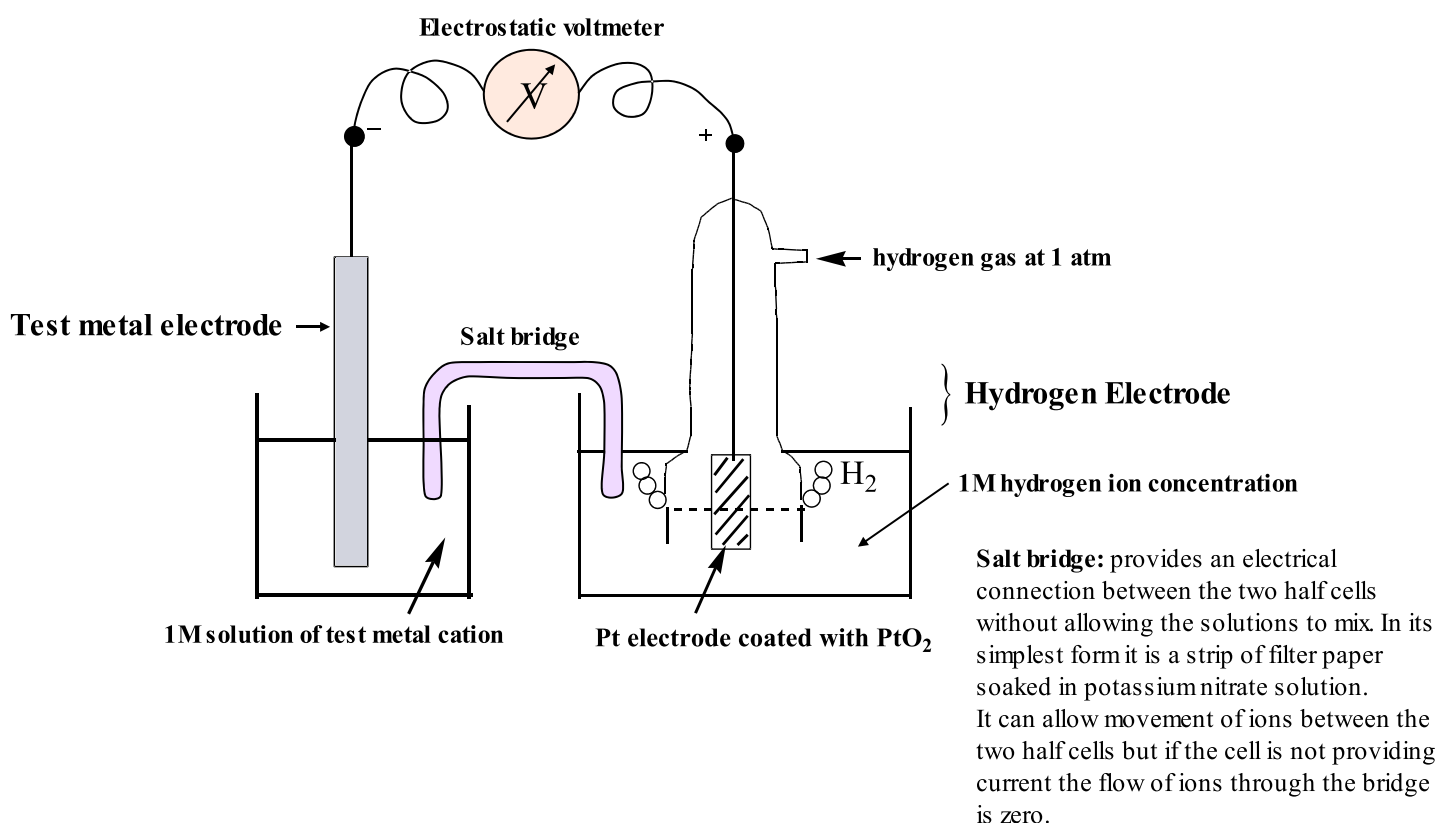
## Redox Equilibria

The magnitude of the metal electrode potential depends on the ionisation energy of the element, the temperature of the solution and the concentration of metal ions in the solution.

If the metal is a reactive metal it will ionise readily and give a *high* electrode potential. An increase in solution temperature facilitates ionisation resulting in an *increase* in electrode potential. An increase in the concentration of metal ions in solution moves the equilibrium to the left *decreasing* electrode potential.

In order to compare the electrode potentials of metals and other species, the temperature is standardised at **25°C** and the solution concentration at **1 mole per dm<sup>3</sup>**. The resulting electrode potential value is referred to as the **standard electrode potential,  $E^\ominus$** .

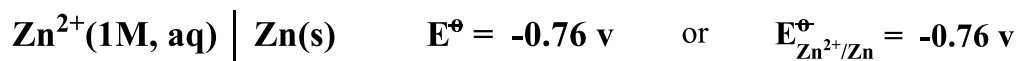
The absolute  $E^\ominus$  value of a *single* electrode (a **half cell**) cannot be measured. Instead, the half cell is connected to a second half cell (a *reference electrode*), to provide a **galvanic** (or **voltaic**) cell, and the emf (electromotive force) of this cell is measured using an *electrostatic voltmeter* (ie, a meter which measures the voltage but takes very little current from the cell). To ensure uniformity the reference electrode is the **standard hydrogen electrode**. By convention this electrode is given a potential of 0.00 volt so that when it is connected to the test electrode, the emf of the resulting galvanic cell can be taken as the standard electrode potential of the test electrode.



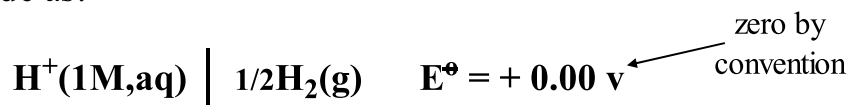
## Redox Equilibria

If zinc was the test electrode it would form the negatively charged electrode and the hydrogen electrode would be the positively charged electrode. The reading on the voltmeter would be 0.76 volt. This is the standard electrode potential of zinc.

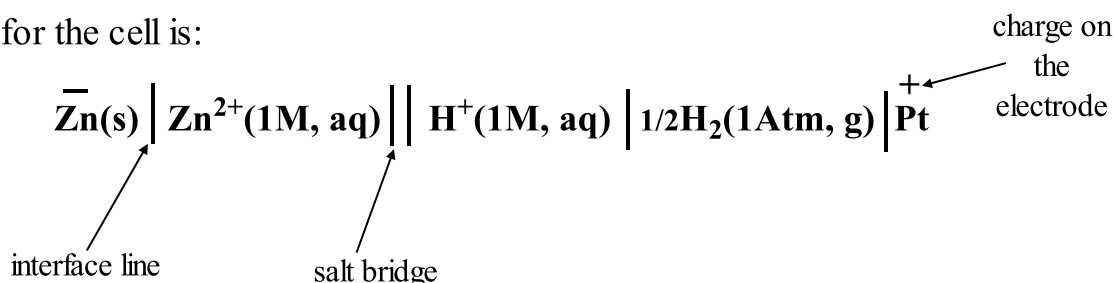
In shorthand we can represent this information as follows:



And the hydrogen electrode as:



The shorthand for the cell is:



It is convention to write the negatively charged electrode on the **left** in the shorthand notation. Then,

$$\begin{aligned} E^\ominus_{\text{cell}} &= E^\ominus_{\text{right hand electrode}} - E^\ominus_{\text{left hand electrode}} \\ &= +0.00 \text{ v} - (-0.76 \text{ v}) = 0.76 \text{ v} \end{aligned}$$

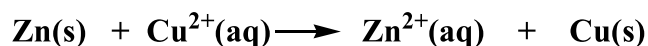
The following is a list of metals with their corresponding standard electrode potential values.

Metal Electrode System	$E^\ominus$ volts
$\text{Li}^+(\text{aq}) + \text{e}^- \rightleftharpoons \text{Li(s)}$	-3.04
$\text{K}^+(\text{aq}) + \text{e}^- \rightleftharpoons \text{K(s)}$	-2.92
$\text{Ca}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Ca(s)}$	-2.87
$\text{Na}^+(\text{aq}) + \text{e}^- \rightleftharpoons \text{Na(s)}$	-2.71
$\text{Mg}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Mg(s)}$	-2.38
$\text{Al}^{3+}(\text{aq}) + 3\text{e}^- \rightleftharpoons \text{Al(s)}$	-1.66
$\text{Zn}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Zn(s)}$	-0.76
$\text{Fe}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Fe(s)}$	-0.44
$\text{Ni}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Ni(s)}$	-0.25
$\text{Pb}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Pb(s)}$	-0.13
$(2\text{H}^+(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{H}_2(\text{g}))$	0.00
$\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Cu(s)}$	+0.34
$\text{Ag}^+(\text{aq}) + \text{e}^- \rightleftharpoons \text{Ag(s)}$	+0.80
$\text{Hg}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Hg(s)}$	+0.85

This list is known as an *electrochemical serie*. It is similar but not identical in all respects to the *reactivity serie*. The electrochemical serie allows us to predict the relative reactivities of the elements in aqueous solution. The higher up the serie the more reactive.

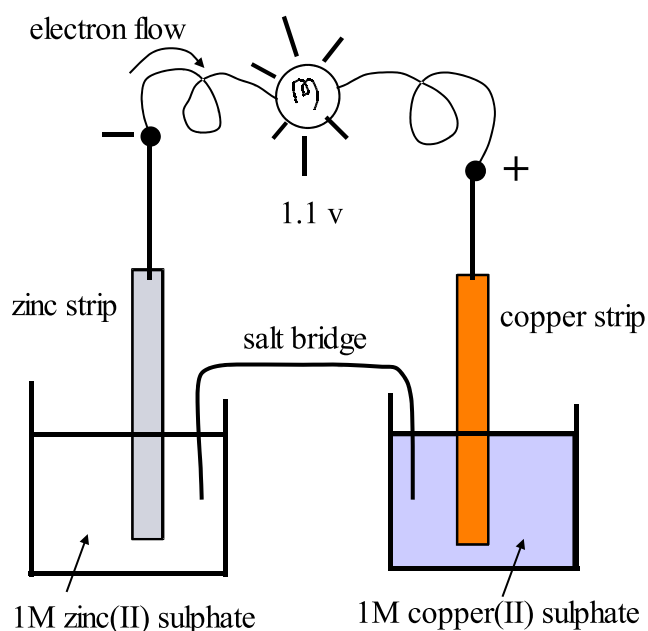
## Redox Equilibria

Looking at the electrochemical series we see that zinc is above copper. This tells us that in aqueous solution zinc is more reactive than copper. Zinc has a greater tendency to give up electrons and form zinc ions than copper has a tendency to form copper ions. This is clearly demonstrated when a clean strip of zinc is placed in a solution of copper sulphate. Quite quickly the zinc becomes coated in metallic copper as a result of this redox reaction:

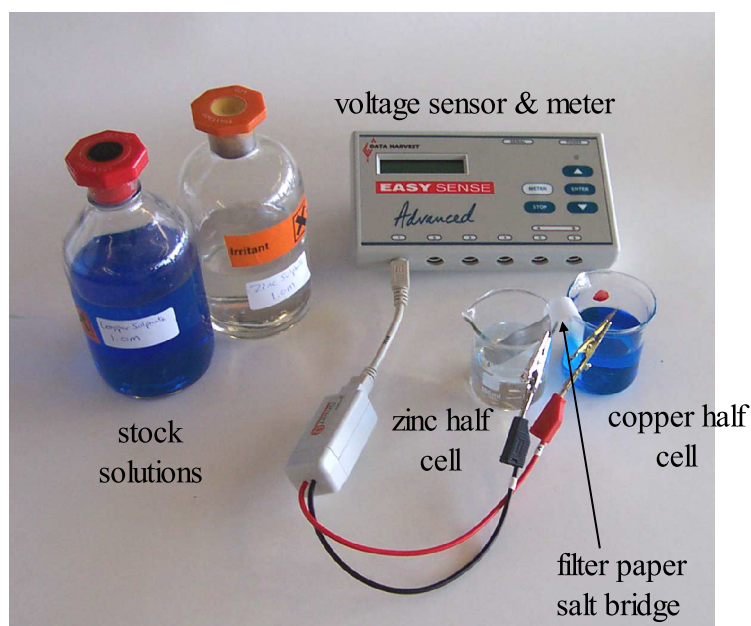


The zinc is giving up electrons to the copper ions. The zinc is oxidised and the copper reduced.

A further illustration would be to construct zinc and copper half cells and connect them via a salt bridge and voltmeter or small torch bulb. The meter would register just over 1 volt and there would be sufficient electrical energy to illuminate the torch bulb. This arrangement is known as a Daniell cell after the inventor, [John Frederic Daniell](#) (1790 -1845). It was the first reliable source of electric current.



$$\begin{aligned} E^\circ_{\text{cell}} &= E^\circ_{\text{right hand electrode}} - E^\circ_{\text{left hand electrode}} \\ &= E^\circ_{\text{copper}} - E^\circ_{\text{zinc}} = +0.34 - (-0.76) = 1.10 \text{ volts} \end{aligned}$$



A simple laboratory arrangement

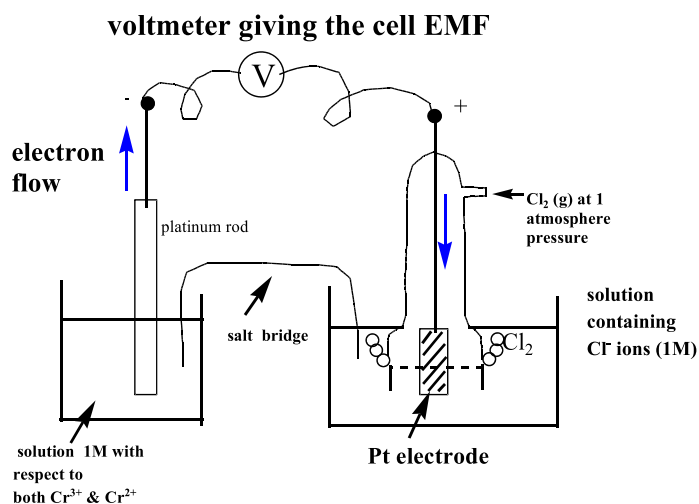
## Redox Equilibria

The list of standard electrode potentials given previously features metal electrodes only. The list can be extended by including **non-metals** and **ionic** systems:

eg,	<b>Metal Electrode System</b>	<b>E° volts</b>
	$\text{Li}^+(\text{aq}) + \text{e}^- \rightleftharpoons \text{Li}(\text{s})$	-3.04
	$\text{K}^+(\text{aq}) + \text{e}^- \rightleftharpoons \text{K}(\text{s})$	-2.92
	$\text{Ca}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Ca}(\text{s})$	-2.87
	$\text{Na}^+(\text{aq}) + \text{e}^- \rightleftharpoons \text{Na}(\text{s})$	-2.71
	$\text{Mg}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Mg}(\text{s})$	-2.38
	$\text{Al}^{3+}(\text{aq}) + 3\text{e}^- \rightleftharpoons \text{Al}(\text{s})$	-1.66
	$\text{Zn}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Zn}(\text{s})$	-0.76
	$\text{Fe}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Fe}(\text{s})$	-0.44
	$\text{Cr}^{3+}(\text{aq}) + \text{e}^- \rightleftharpoons \text{Cr}^{2+}(\text{aq})$	-0.41
	$\text{Ni}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Ni}(\text{s})$	-0.25
	$\text{Pb}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Pb}(\text{s})$	-0.13
	$(2\text{H}^+(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{H}_2(\text{g}))$	00.0)
	$\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Cu}(\text{s})$	+0.34
	$\text{I}_2(\text{s}) + 2\text{e}^- \rightleftharpoons 2\text{I}^-(\text{aq})$	+0.54
	$\text{Ag}^+(\text{aq}) + \text{e}^- \rightleftharpoons \text{Ag}(\text{s})$	+0.80
	$\text{Hg}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Hg}(\text{s})$	+0.85
	$\text{Cl}_2(\text{g}) + 2\text{e}^- \rightleftharpoons 2\text{Cl}^-(\text{aq})$	+1.36

(NB: you will find more extensive lists in your data book. Also see *homework section*.)

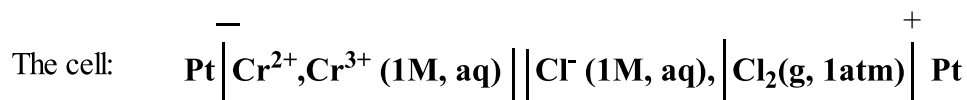
Lets construct a chromium/chlorine cell!



If this strange looking cell was constructed what emf would it produce?

Notice that in order to feed electrons to or from the chromium system an inert **platinum** electrode dips into the solution of chromium ions (we cannot use metallic chromium since that would complicate the arrangement by providing additional electrode systems).

The chlorine electrode is similar to the hydrogen electrode in construction.



$$\text{cell EMF} = E^\circ_{\text{Cl}_2/\text{Cl}^-} - E^\circ_{\text{Cr}^{3+}/\text{Cr}^{2+}}$$

$$\text{cell emf} = +1.36 - (-0.41) = 1.36 + 0.41 = 1.77 \text{ v}$$

This is a substantial voltage but a, potentially, very hazardous cell!

## Predicting Reactions

The value of the electrochemical series is that, just by noting where metals or non-metals occur in the series, it enables us to *predict* whether a reaction is likely to occur between particular reactants in aqueous solution.

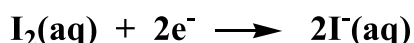
eg,

If a clean piece of magnesium is placed in a beaker of iodine solution are the two likely to react?

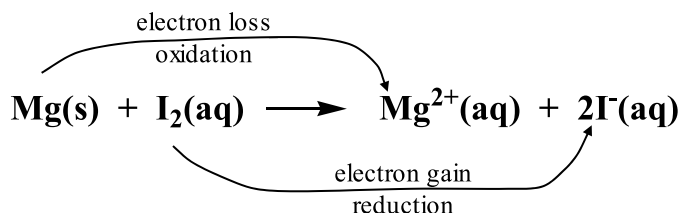
In its reactions magnesium can convert to magnesium ions by giving up electrons.



Iodine, in its reactions, can convert to iodide by accepting electrons.



Look at the electrochemical series and see whether the magnesium system  $\text{Mg}/\text{Mg}^{2+}$  has the more negative electrode potential. If so, it will be higher up in the series than the iodine system  $\text{I}_2/2\text{I}^{-}$  and will be more reducing. If this is the case (and it is!) we can predict that magnesium *will* reduce iodine in aqueous solution.



We also expect a colour change from brown (due to aqueous iodine) to colourless (magnesium & iodide ions).

We could also perform a quick calculation to see if the cell emf, involving these two systems, is a *positive* value. It will be if the above redox reaction is feasible.

ie,

$$\text{Mg(s)} \parallel \text{Mg}^{2+}(\text{aq}) \parallel \text{I}^{-}(\text{aq}), \text{I}_2(\text{aq}) \parallel \text{Pt}^{+} \quad E_{\text{cell}} = +0.54 - (-2.38) \text{ v} = +2.92 \text{ v}$$

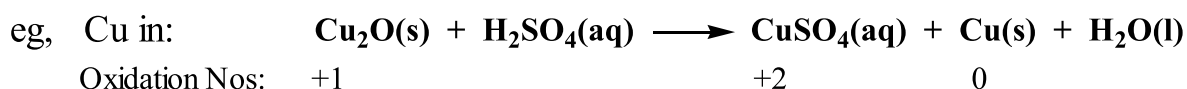
Furthermore, for a reaction to be feasible  $\Delta G$  must be negative.

Now, for a redox reaction in an electrochemical cell,

$\Delta G^{\ominus} = -zFE^{\ominus}$  ( $z$  = electrons transferred per mol of reaction,  $F$  = Faraday constant 96500C). From which,  $\Delta G = -2 \times 96500 \times (+2.92) = -563,560 \text{ Jmol}^{-1}$ . This high negative  $\Delta G$  value indicates a highly feasible reaction since a large amount of energy is potentially available to perform useful work!

# Disproportionation Reactions

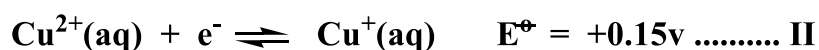
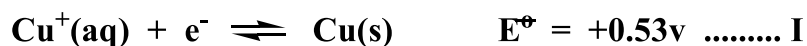
Disproportionation is where an element undergoes both oxidation and reduction in the same reaction.



Here, the copper(I) is oxidised *and* reduced.  
How can we account for this?

In this reaction there are two competing redox equilibria involving the disproportionating specie copper(I).

ie,

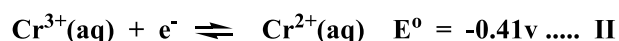
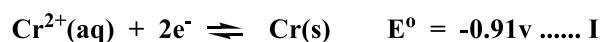


Equilibrium II has the more negative electrode potential and is therefore more reducing. It will provide electrons to equilibrium I. This means that some of the copper(I) will convert to copper(II) and the electron generated will be used to convert more of the copper(I) to copper metal. As the reaction goes to completion, half of the copper(I) is converted to copper(II) and the other half to metallic copper.

If you are faced with providing explanations like this you will need to remember that the disproportionating specie must be present in the half equations as both oxidant and reductant. In the above half equations copper(I) is acting as oxidising agent in equation I (since it is accepting an electron) and reducing agent in equation II (since it is giving up an electron).

Is this disproportionation feasible,  $3\text{Cr}^{2+}(\text{aq}) \longrightarrow 2\text{Cr}^{3+}(\text{aq}) + \text{Cr}$  ? We need two half equations, one in which chromium(II) is reduced and one in which it is oxidised.

ie,

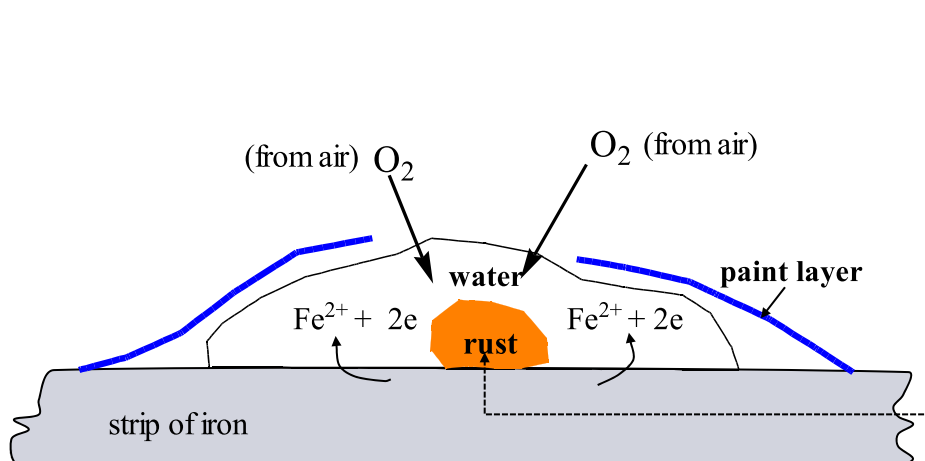
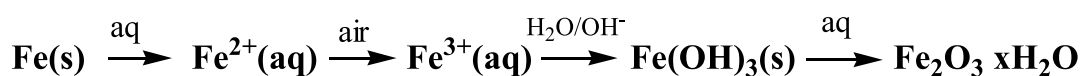


System I is the more negative. It will provide electrons to system II. This is not what we want. The given disproportionation would not occur, in fact, it would tend to go in the opposite direction; chromium(III) and chromium metal reacting to give chromium(II)!

## Corrosion

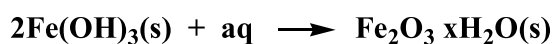
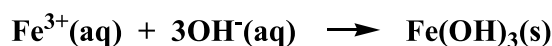
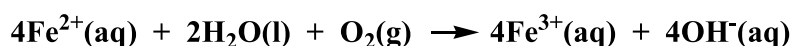
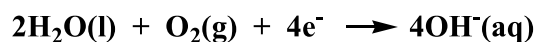
The corrosion of a metal is an electrolytic process in which the metal loses electrons and reacts with substances in the environment forming compounds (the corrosion products).

The most familiar corrosion process is the rusting of iron.  
ie,



The diagram illustrates a section of damaged paint film on a piece of painted iron. Moisture has got under the layer of paint and the iron is beginning to rust.

### Summary of the chemical processes:

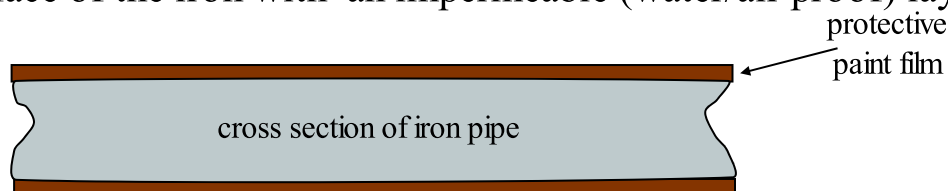


**RUST**



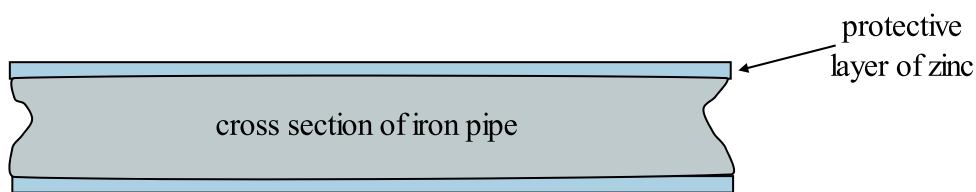
### How can the corrosion of iron be prevented?

1. Cover the surface of the iron with an impermeable (water/air proof) layer of paint.



This is a good solution providing the paint film does not become damaged or deteriorate so that water and air can make contact with the metal.

2. Cover the surface of the iron with a more reactive metal such as zinc.



The zinc can be applied by dipping the iron in molten zinc. The iron is said to be **galvanised**.



galvanised watering can

Newly galvanised iron objects have a bright, shiny, appearance and the crystalline structure of the zinc is clearly visible.

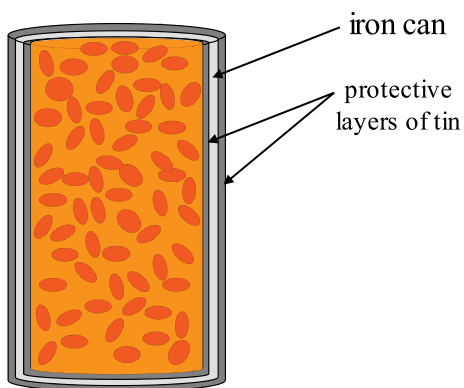
Zinc has a more negative  $E^\ominus$  value than iron and will corrode before the iron. Even when the surface becomes damaged the zinc will afford some protection because it will form a cell with the iron and undergo oxidation in preference to the iron.

An alternative to dipping, is to attach blocks of zinc or magnesium to the iron which act as **sacrificial anodes**, corroding away in preference to the iron. This is a useful procedure for underground pipelines and ships hulls.

3. Cover the surface of the iron with a *less* reactive metal.

If **tin** is used the process is called ***tinning***.

eg,



a tin of baked beans

(not to scale ---

& the tin accounts for only about 0.5% of the metal can!)

The tin provides a tough, malleable and non-toxic coating which protects the underling iron from reaction with air, water and dilute acid solutions.

The disadvantage of tin is that once its surface becomes damaged the iron underneath is no longer protected because the iron, being more reactive ( $-0.44\text{v}$ ), oxidises in preference to the tin ( $-0.14\text{v}$ ).

The tin is applied to the iron by dipping in molten tin or by electroplating. The latter gives a more uniform coating

## Storage cells.

Batteries are known as storage cells. They are packed with chemicals which, at the flick of a switch, react to produce electrical energy. There are two main types, ***primary cells*** (disposable cells) and ***secondary cells*** (rechargeable cells).

### Primary Cells.

Used in devices such as:

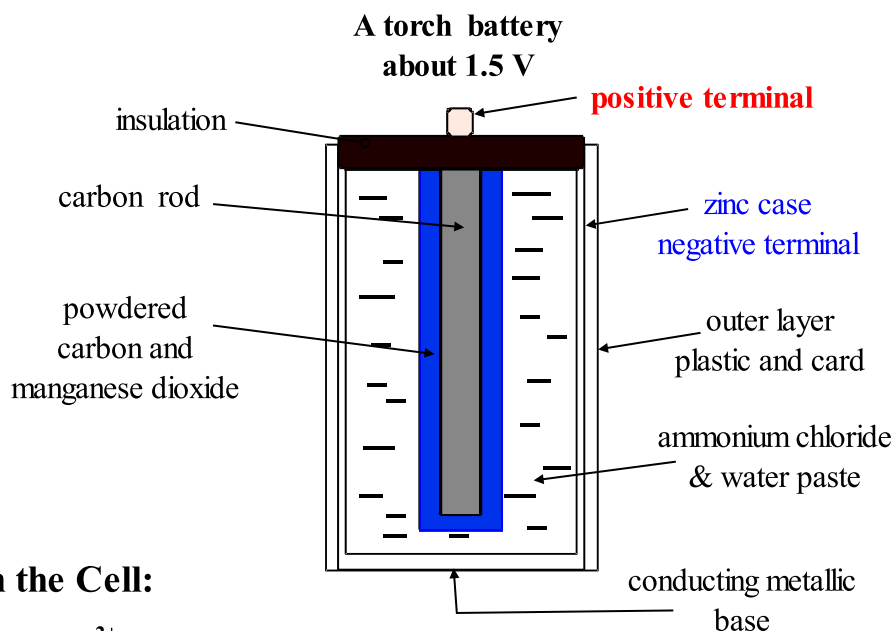


The common torch battery provides electrical energy when metallic zinc converts to zinc ions and gives up electrons.

# Redox Equilibria



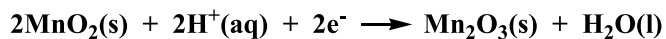
Torch batteries



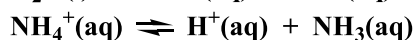
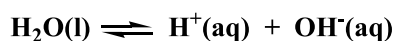
## Chemical Changes within the Cell:

zinc case: negative terminal  $\text{Zn(s)} \rightarrow \text{Zn}^{2+} + 2\text{e}^-$

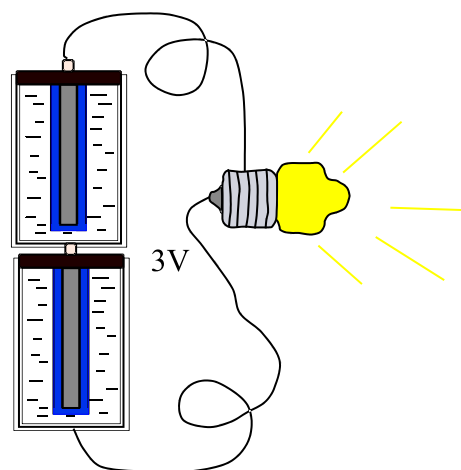
The zinc ions complex with ammonia which is liberated in the region of the carbon rod:  $\text{Zn}^{2+} + 2\text{NH}_3 \rightarrow [\text{Zn}(\text{NH}_3)_2]^{2+}$   
Electrons flow round the external circuit to the positive terminal. At the positive terminal, which is the carbon rod and manganese dioxide, the electrons reduce the dioxide to manganese(III) oxide.



Hydrogen ions are available from water and from the dissociation of ammonium ions.



Ammonia molecules complex with the zinc ions (see above).



The performance of this type of cell decreases with use.  
The chemicals are used up. The cell cannot be recharged.

## Secondary Cells

Used in :



and

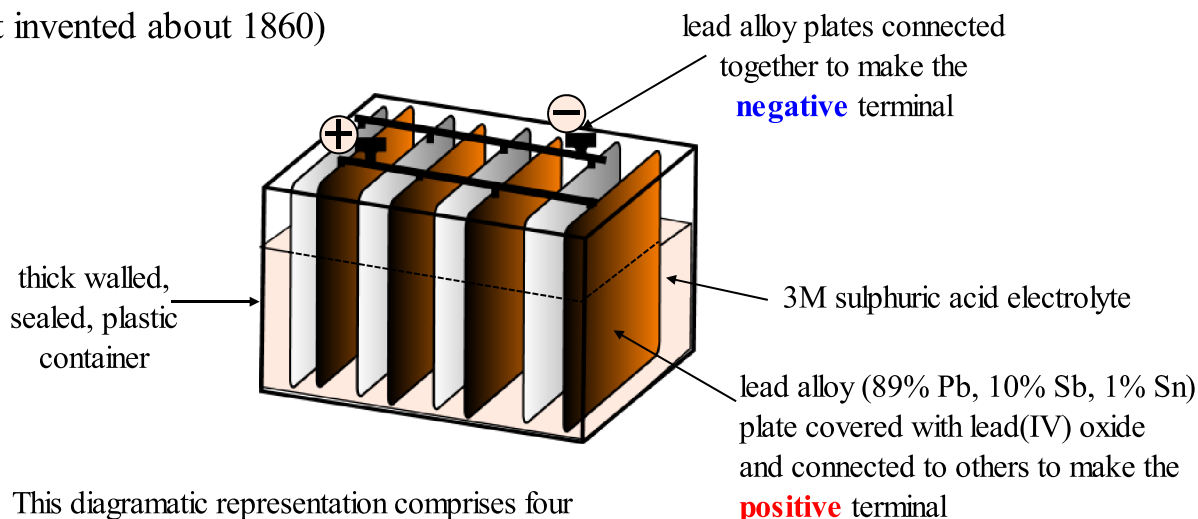


## Redox Equilibria

The lead acid accumulator is the battery of choice in most cars and lorries. For computers, cameras, shavers, toys and other household objects smaller rechargeable batteries such as nickel-cadmium, nickel-metal hydride and lithium ion are used.

### The Lead-acid Accumulator:

(first invented about 1860)

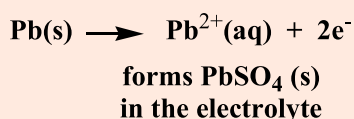


This diagrammatic representation comprises four pairs of plates (4 cells). Lead accumulators used in cars often have six cells each providing about 2V.

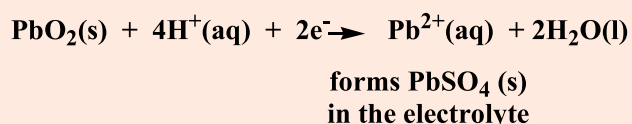
When the terminals are connected to an electrical device, such as headlights or starter motor, electrons flow through the device as they move between the two sets of plates. Both sets of plates become coated with insoluble lead sulphate and eventually, the electrical output falls to a low value. When this happens the battery may be *recharged* by applying electrical energy, from a *battery charger*. This converts lead sulphate back into, lead at the negative plate, and lead dioxide at the positive plate.

#### Discharge reactions --- by connecting to electrical device

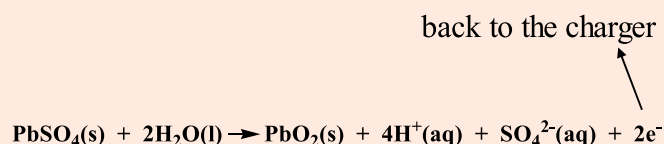
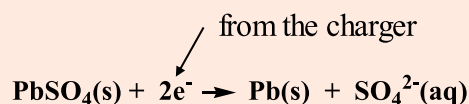
**At the negative terminal:**



**At the positive terminal:**



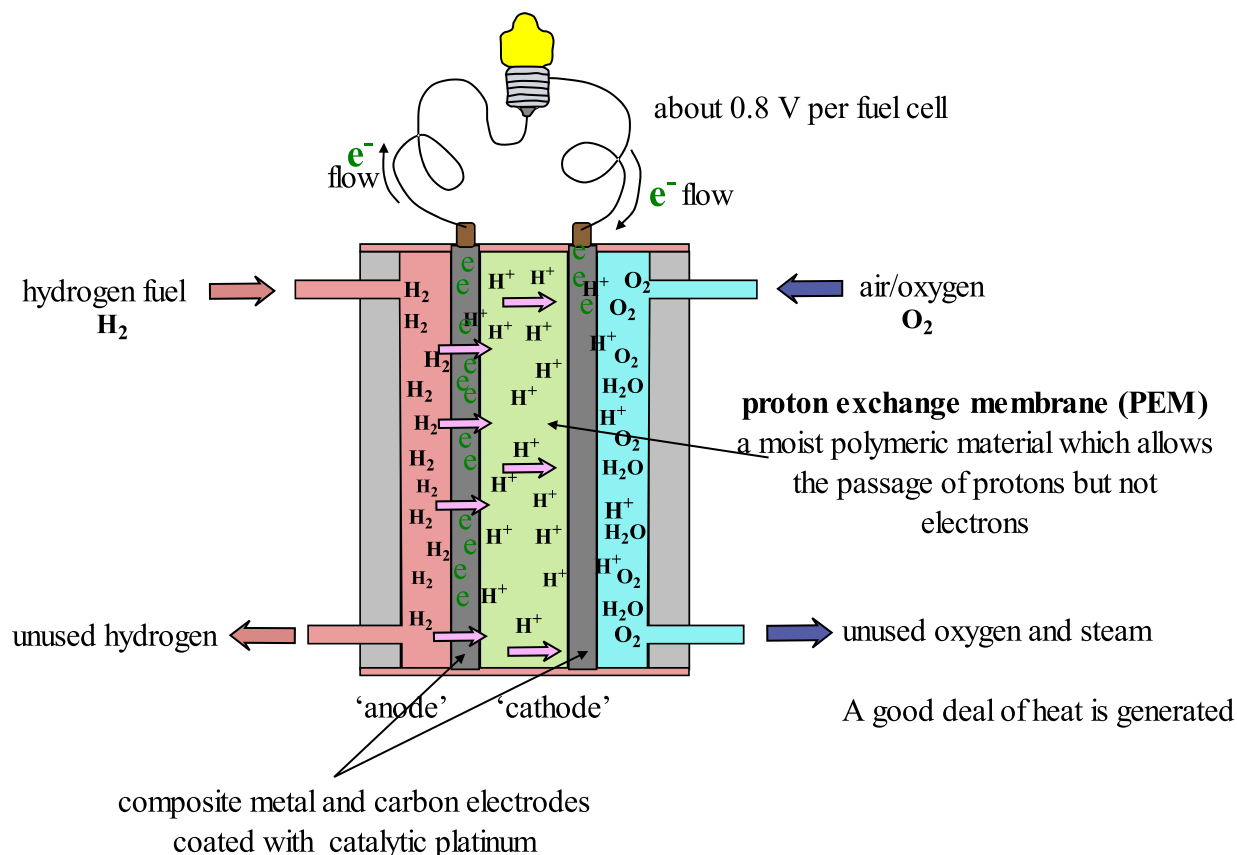
#### Charging reactions --- by connecting to battery charger:



## Fuel Cells.

The fuel cell is a type of battery. However, it differs from the primary and secondary cells, describe previously, in that the chemicals required to generate electric current are not stored within the cell. The reductant and oxidant are fed into the cell from external stores. Providing these external supplies of chemicals do not dry up the cell can operate continuously and indefinitely.

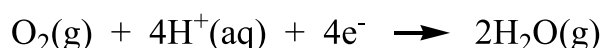
eg,



On the Pt catalyst surface of the anode, hydrogen molecules dissociate to give electrons and protons. The protons flow through the PEM to the cathode. The electrons accumulate at the anode and flow into the external circuit providing electric current to power some device (an electric light bulb in the diagram above).



On the Pt surface of the cathode, protons, oxygen molecules and electrons (from the external circuit) combine producing water (as steam).



### Uses:

Modern space vehicles use fuel cells. The Apollo moon probes used earlier versions of the hydrogen-oxygen fuel cells.

Modern submarines use fuel cells and prototype cars and buses have been designed and built to run off fuel cells.

Large 200 kW fuel cell stacks are available for use in hospitals, universities and factories.

### Advantages and Disadvantages:

The main *advantages* of fuel cells are,

- (i) readily available fuel (hydrogen) and oxidant (oxygen or air),
- (ii) little or no harmful emissions,
- (iii) reliable and efficient (a comparable fuel cell stack is about 1.7 times more efficient than a standard diesel engine).

The main *disadvantages* of fuel cells are,

- (i) those required for cars and buses are bulky and expensive,
- (ii) the gaseous fuel and oxidant are more difficult to store and transport than traditional *liquid* fuels (eg, petrol and diesel).

It is possible to produce the hydrogen gas from hydrogen rich liquid compounds stored in tanks on the vehicle. The gas is then fed directly to the fuel cell. This reduces the possibility of accidental fire associated with storage and transport of a highly flammable gas. However, this would increase the overall size of the power unit.

- (iii) hydrogen is highly flammable and potentially explosive so there are special safety issues to be addressed to avoid serious accidents.